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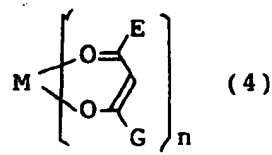
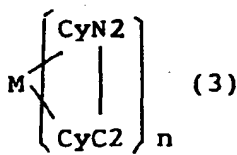
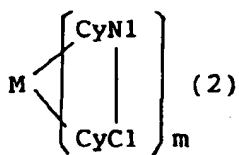
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(54) **Metal coordination compound, luminescence device and display apparatus**

(57) An electroluminescence device having a layer containing a specific metal coordination compound is provided. The metal coordination compound is represented by formula (1) below:



wherein M is a metal atom of Ir, Pt, Rh or Pd; L and L' are mutually different bidentate ligands; m is 1, 2 or 3 and n is 0, 1 or 2 with the proviso that m+n is 2 or 3; a partial structure ML_m is represented by formula (2) shown below and a partial structure ML'_n is represented by formula (3) or (4) shown below:

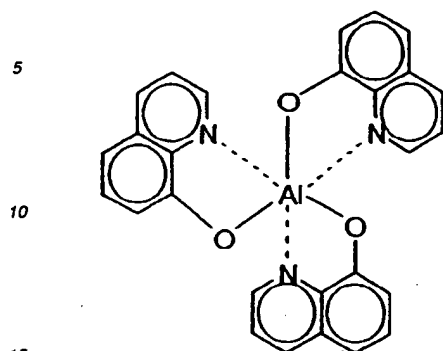
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The metal coordination compound of the formula (1) is characterized by having at least one aromatic substituent for at least one of CyN1, CyN2, CyC1 and CyC2. The metal coordination compound having the aromatic substituent is effective in providing high-efficiency luminescence, long-term high luminance, and less deterioration by current passing.

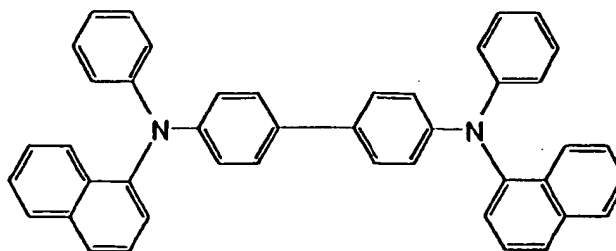
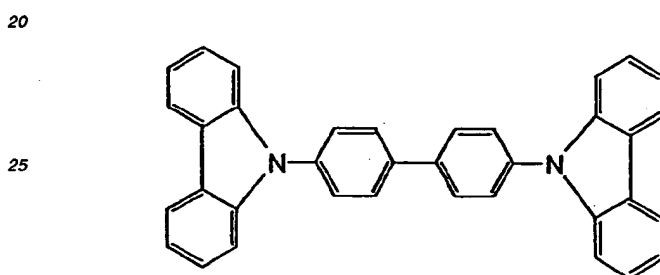
Description

FIELD OF THE INVENTION AND RELATED ART

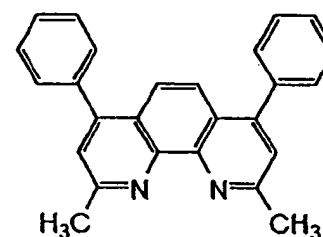
- 5 **[0001]** The present invention relates to a luminescence device, a display apparatus and a metal coordination compound therefor. More specifically, the present invention relates to a luminescence device employing an organic metal coordination compound having a formula (1) appearing hereinafter as a luminescence material so as to allow stable luminescence efficiency, a display apparatus including the luminescence device and the metal coordination compound adapted for use in the luminescence device.
- 10 **[0002]** An organic electroluminescence (EL) device has been extensively studied as a luminescence device with a high responsiveness and high efficiency.
- [0003]** The organic EL device generally has a sectional structure as shown in Figure 1A or 1B (e.g., as described in "Macromol. Symp.", 125, pp. 1 - 48 (1997)).
- 15 **[0004]** Referring to the figures, the EL device generally has a structure including a transparent substrate 15, a transparent electrode 14 disposed on the transparent substrate 15, a metal electrode 11 disposed opposite to the transparent electrode 14, and a plurality of organic (compound) layers disposed between the transparent electrode 14 and the metal electrode 11.
- [0005]** Referring to Figure 1, the EL device in this embodiment has two organic layers including a luminescence layer 12 and a hole transport layer 13.
- 20 **[0006]** The transparent electrode 14 may be formed of a film of ITO (indium tin oxide) having a larger work function to ensure a good hole injection performance into the hole transport layer. On the other hand, the metal electrode 11 may be formed of a layer of aluminum, magnesium, alloys thereof, etc., having a smaller work function to ensure a good electron injection performance into the organic layer(s).
- [0007]** These (transparent and metal) electrodes 14 and 11 may be formed in a thickness of 50 - 200 nm.
- 25 **[0008]** The luminescence layer 12 may be formed of, e.g., aluminum quinolinol complex (representative example thereof may include Alq3 described hereinafter) having an electron transporting characteristic and a luminescent characteristic. The hole transport layer 13 may be formed of, e.g., triphenyldiamine derivative (representative example thereof may include α -NPD described hereinafter) having an electron donating characteristic.
- [0009]** The above-described EL device exhibits a rectification characteristic, so that when an electric field is applied between the metal electrode 11 as a cathode and the transparent electrode 14 as an anode, electrons are injected from the metal electrode 11 into the luminescence layer 12 and holes are injected from the transparent electrodes 14.
- 30 **[0010]** The thus-injected holes and electrons are recombined within the luminescence layer 12 to produce excitons, thus causing luminescence. At that time, the hole transport layer 13 functions as an electron-blocking layer to increase a recombination efficiency at the boundary between the luminescence layer 12 and the hole transport layer 13, thus enhancing a luminescence efficiency.
- 35 **[0011]** Referring to Figure 1B, in addition to the layers shown in Figure 1A, an electron transport layer 16 is disposed between the metal electrode 11 and the luminescence layer 12, whereby an effective carrier blocking performance can be ensured by separating functions of luminescence, electron transport and hole transport, thus allowing effective luminescence.
- 40 **[0012]** The electron transport layer 16 may be formed of, e.g., oxadiazole derivatives.
- [0013]** In ordinary organic EL devices, fluorescence caused during a transition of luminescent center molecule from a singlet excited state to a ground state is used as luminescence.
- [0014]** On the other hand, not the above fluorescence (luminescence) via singlet exciton, phosphorescence (luminescence) via triplet exciton has been studied for use in organic EL device as described in, e.g., "Improved energy transfer in electrophosphorescent device" (D.F. O'Brien et al., Applied Physics Letters, Vol. 74, No. 3, pp. 442 - 444 (1999)) and "Very high-efficiency green organic light-emitting devices based on electrophosphorescence" (M.A. Baldo et al., Applied Physics Letters, Vol. 75, No. 1, pp. 4 - 6 (1999)).
- 45 **[0015]** The EL devices shown in these documents may generally have a sectional structure shown in Figure 1C.
- [0016]** Referring to Figure 1C, four organic layers including a hole transfer layer 13, a luminescence layer 12, an exciton diffusion-prevention layer 17, and an electron transport layer 16 are successively formed in this order on the transparent electrode (anode) 14.
- 50 **[0017]** In the above documents, higher efficiencies have been achieved by using four organic layers including a hole transport layer 13 of α -NPD (shown below), an electron transport layer 16 of Alq3 (shown below), an exciton diffusion-prevention layer 17 of BPC (shown below), and a luminescence layer 12 of a mixture of CPB (shown below) as a host material with Ir(ppy)₃ (shown below) or PtOEP (shown below) as a guest phosphorescence material doped into CBP at a concentration of ca. 6 wt. %.
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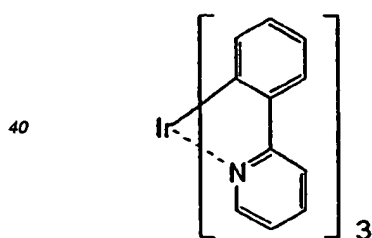
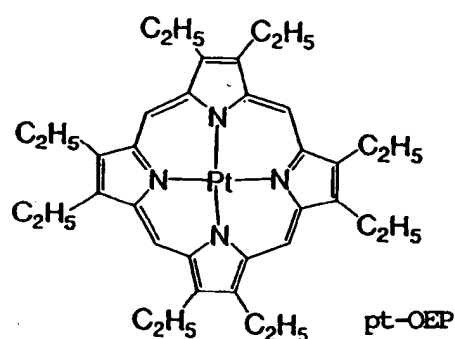
Alq3

 α -NPD

CBP



BCP

Ir(ppy)₃

pt-OEP

Alq3: tris(8-hydroxyquinoline) aluminum (aluminum-quinolinol complex),
 α -NPD: N4,N4'-di-naphthalene-1-yl-N4,N4'-diphenyl-biphenyl-4,4'-diamine (4,4'-bis[N-(1-naphthyl)-N-phenyl-amino]biphenyl),
 CBP: 4,4'-N,N'-dicarbazole-biphenyl,
 BCP: 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline,
 Ir(ppy)₃: fac tris(2-phenylpyridine)iridium (iridium-phenylpyridine complex), and
 PtOEP: 2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphine platinum (platinum-octaethyl porphine complex).

[0018] The phosphorescence (luminescence) material used in the luminescence layer 12 has attracted notice. This

is because the phosphorescence material is expected to provide a higher luminescence efficiency in principle.

[0019] More specifically, in the case of the phosphorescence material, excitons produced by recombination of carriers comprise singlet excitons and triplet excitons presented in a ratio of 1:3. For this reason, when fluorescence caused during the transition from the singlet excited state to the ground state is utilized, a resultant luminescence efficiency is 25 % (as upper limit) based on all the produced excitons in principle.

[0020] On the other hand, in the case of utilizing phosphorescence caused during transition from the triplet excited state, a resultant luminescence efficiency is expected to be at least three times that of the case of fluorescence in principle. In addition thereto, if intersystem crossing from the singlet excited state (higher energy level) to the triplet excited state is taken into consideration, the luminescence efficiency of phosphorescence can be expected to be 100 % (four times that of fluorescence) in principle.

[0021] The use of phosphorescence based on transition from the triplet excited state has also been proposed in, e. g., Japanese Laid-Open Patent Application (JP-A) 11-329739, JP-A 11-256148 and JP-A 8-319482.

[0022] However, the above-mentioned organic EL devices utilizing phosphorescence have accompanied with a problem of luminescent deterioration particularly in an energized state.

[0023] The reason for luminescent deterioration has not been clarified as yet but may be attributable to such a phenomenon that the life of triplet exciton is generally longer than that of singlet exciton by at least three digits, so that molecule is placed in a higher-energy state for a long period to cause reaction with ambient substance, formation of exciplex or excimer, change in minute molecular structure, structural change of ambient substance, etc.

[0024] Accordingly, the (electro)phosphorescence EL device is expected to provide a higher luminescence efficiency as described above, while the EL device is required to suppress or minimize the luminescent deterioration in energized state. Further, a luminescence center material for the EL device is required to allow high-efficiency luminescence and exhibit a good stability.

SUMMARY OF THE INVENTION

[0025] An object of the present invention is to provide a luminescence device capable of providing a high-efficiency luminescent state at a high brightness (or luminance) for a long period while minimizing the deterioration in luminescence in energized state.

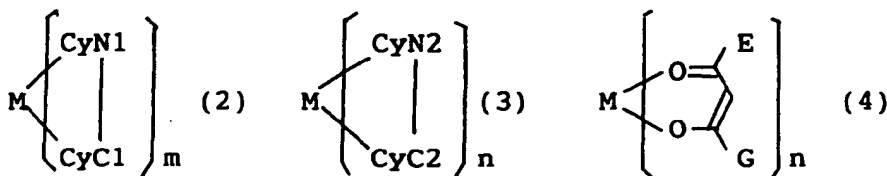
[0026] Another object of the present invention is to provide a display apparatus including the luminescence device.

[0027] A further object of the present invention is to provide a metal coordination compound as a luminescence center material suitable for an organic layer for the luminescence device.

[0028] According to the present invention, there is provided a metal coordination compound (metal complex), particularly an iridium complex, characterized by having at least one aromatic substituent. More specifically, there is provided a metal coordination compound represented by formula (1) below:



wherein M is a metal atom of Ir, Pt, Rh or Pd; L and L' are mutually different bidentate ligands; m is 1, 2 or 3 and n is 0, 1 or 2 with the proviso that m+n is 2 or 3; a partial structure ML_m is represented by formula (2) shown below and a partial structure ML'_n is represented by formula (3) or (4) shown below:



wherein CyN1 and CyN2 are each cyclic group capable of having a substituent, including a nitrogen atom and bonded to the metal atom M via the nitrogen atom; CyC1 and CyC2 are each cyclic group capable of having a substituent, including a carbon atom and bonded to the metal atom M via the carbon atom with the proviso that the cyclic group CyN1 and the cyclic group CyC1 are bonded to each other via a covalent bond and the cyclic group CyN2 and the

cyclic group CyC2 are bonded to each other via a covalent bond;

the optional substituent of the cyclic groups is selected from a halogen atom, cyano group, a nitro group, a trialkylsilyl group of which the alkyl groups are independently a linear or branched alkyl group having 1 to 8 carbon atoms, a linear or branched alkyl group having 1 to 20 carbon atoms of which the alkyl group can include one or non-
 5 neighboring two or more methylene groups that can be replaced with -O-, -S-, -CO-, -CO-O-, -O-CO-, -CH=CH- or -C≡C-, and the alkyl group can include a hydrogen atom that can be optionally replaced with a fluorine atom; or an aromatic group capable of having a substituent which is selected from an aromatic group capable of having a substituent (that is a halogen atom, a cyano atom, a nitro atom, a linear or branched alkyl group having 1 to 20 carbon atoms of which the alkyl group can include one or non-neighboring two or more methylene groups that can be replaced with
 10 -O-, -S-, -CO-, -CO-O-, -O-CO-, -CH=CH- or -C≡C-, and the alkyl group can include a hydrogen atom that can be optionally replaced with a fluorine atom), a halogen atom, a cyano atom, a nitro atom, and a linear or branched alkyl group having 1 to 20 carbon atoms (of which the alkyl group can include one or non-neighboring two or more methylene groups that can be replaced with -O-, -S-, -CO-, -CO-O-, -O-CO-, -CH=CH- or -C≡C-, and the alkyl group can include a hydrogen atom that can be optionally replaced with a fluorine atom);

15 E and G are independently a linear or branched alkyl group having 1 to 20 carbon atoms of which the alkyl group can include a hydrogen atom that can be optionally replaced with a fluorine atom, or an aromatic group capable of having a substituent (that is a halogen atom, a cyano atom, a nitro atom, a trialkylsilyl group of which the alkyl groups are independently a linear or branched alkyl group having 1 - 8 carbon atoms, a linear or branched alkyl group having 1 to 20 carbon atoms of which the alkyl group can include one or non-neighboring two or more methylene groups that
 20 can be replaced with -O-, -S-, -CO-, -CO-O-, -O-CO-, -CH=CH- or -C≡C-, and the alkyl group can include a hydrogen atom that can be optionally replaced with a fluorine atom; and

the cyclic groups CyN1, CyN2, CyC1 and CyC2 have at least one aromatic substituent capable of having a substituent which is selected from an aromatic group capable of having a substituent (that is a halogen atom, a cyano atom, a nitro atom, a linear or branched alkyl group having 1 to 20 carbon atoms of which the alkyl group can include
 25 one or non-neighboring two or more methylene groups that can be replaced with -O-, -S-, -CO-, -CO-O-, -O-CO-, -CH=CH- or -C≡C-, and the alkyl group can include a hydrogen atom that can be optionally replaced with a fluorine atom), a halogen atom, a cyano atom, a nitro atom, a linear or branched alkyl group having 1 to 20 carbon atoms of which the alkyl group can include one or non-neighboring two or more methylene groups that can be replaced with -O-, -S-, -CO-, -CO-O-, -O-CO-, -CH=CH- or -C≡C-, and the alkyl group can include a hydrogen atom that can be
 30 optionally replaced with a fluorine atom).

[0029] In the formula (1), M may preferably be Ir as described above, and n may preferably be 0.

[0030] In the formula (2), CyN1 and CyC1 may preferably be any one of the following combinations:

CyN1	CyC1
pyridyl	naphthyl
pyridyl	thienyl
pyridyl	benzothienyl

40 [0031] The present invention also provides an electroluminescence device, comprising: a pair of electrodes disposed on a substrate, and a luminescence unit comprising at least one organic compound disposed between the electrodes, wherein the organic compound comprises a metal coordination compound represented by the above-mentioned formula (1).

[0032] In the electroluminescence device, a voltage is applied between the electrodes to emit light.

45 [0033] In a preferred embodiment of the electroluminescence device, a voltage is applied between the electrodes to emit phosphorescence.

[0034] The present invention further provides a picture display apparatus, comprising an electroluminescence device described above and a means for supplying electric signals to the electroluminescence device.

50 [0035] These and other objects, features and advantages of the present invention will become more apparent upon a consideration of the following description of the preferred embodiments of the present invention taken in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

55 [0036]

Figures 1A, 1B and 1C illustrate embodiments of the luminescence device according to the present invention, respectively.

Figure 2 schematically illustrates a panel structure including an EL device and drive means.

Figures 3A, 3B and 3C show device performances of a luminescence device used in Example 9 appearing hereinafter, wherein Figure 3A shows an electric field strength-current density curve, Figure 3B shows an electric field strength-luminance curve, and Figure 3C shows a luminescence spectrum under application of a voltage of 10 volts.

DETAILED DESCRIPTION OF THE INVENTION

[0037] In the case where the luminescence layer comprises a host material having a carrier-transporting function and a phosphorescent guest material, a process of phosphorescence via triplet excitons may include unit processes as follows:

1. transportation of electrons and holes within a luminescence layer,
2. formation of host excitons,
3. excitation energy transfer between host molecules,
4. excitation energy transfer from the host to the guest,
5. formation of guest triplet excitons, and
6. transition of the guest triplet excitons to the ground state and phosphorescence.

[0038] Desirable energy transfer in each unit process and luminescence are caused in competition with various energy deactivation processes.

[0039] Needless to say, a luminescence efficiency of an organic luminescence device is increased by increasing the luminescence quantum yield of a luminescence center material. In addition thereto, an efficient energy transfer between host material molecules and/or between host material molecule and guest material molecule is also an important factor.

[0040] Further, the above-described luminescent deterioration in energized state may presumably relate to the luminescent center material per se or an environmental change thereof by its ambient molecular structure.

[0041] For this reason, our research group has extensively investigated an effect of use of the metal coordination compound of formula (1) as the luminescent center material and as a result, has found that the metal coordination compound of formula (1) allows a high-efficiency luminescence with a high brightness (luminance) for a long period, and less deterioration in energized state.

[0042] The metal coordination compound represented by the above formula (1) according to the present invention causes phosphorescence (luminescence) and its lowest excited state is believed to be an MLT* (metal-to-ligand charge transfer) excited state or π - π^* excited state in a triplet state. The phosphorescent emission of light (phosphorescence) is caused at the time of transition from such a state to the ground state.

[0043] The metal coordination compound of formula (1) according to the present invention has been found to provide a higher phosphorescence (quantum) yield of 0.05 - 0.9 and a shorter phosphorescence life of 1 - 40 μ sec, as a result of our luminescence experiment based on photoluminescence by photo-excitation.

[0044] The shorter phosphorescence life is necessary to provide a resultant EL device with a higher luminescence efficiency. This is because the longer phosphorescence life increases molecules placed in their triplet excited state which is a waiting state for phosphorescence, thus lowering the resultant luminescence efficiency particularly at a higher current density. Further, an emission wavelength can be controlled by changing appropriately substituents R1 to T6 and species of aromatic group of the metal coordination compound of the formula (1).

[0045] Also from these viewpoints, the metal coordination compound of formula (1) according to the present invention is a suitable luminescent material for an EL device with a higher phosphorescence yield and a shorter phosphorescence life.

[0046] Particularly, by providing an aromatic group as a substituent (i.e., aromatic substituent) of the metal coordination compound of the formula (1), the resultant substituent has π -electron system extended to the outside of the metal coordination compound molecules, thus facilitating energy transfer from a host material and assisting electron/hole transport functions to result in an improved carrier transport performance. Further, in the present invention, the metal coordination compound of the formula (1) may preferably have the cyclic group CyN1 and/or CyN2 having pyridine structure, a pyridine derivative wherein one of CH groups is substituted with N atom, and fine-membered ring structures containing nitrogen atom and/or sulfur atom. By these partial structures, the resultant metal coordination compound of the formula (1) can be synthesized with a high yield and an excellent stability necessary for the luminescence material.

[0047] In addition, as substantiated in Examples appearing hereinafter, it has been confirmed that the metal coordination compound of the formula (1) also exhibited an excellent stability in a durability test by continuous current passage. This may be attributable to a controlled intermolecular interaction of the metal coordination compound of the formula (1) with the host material by introducing the aromatic substituent characterizing the metal coordination compound of the present invention into the metal coordination compound thereby to change an intermolecular interaction. As a result, it becomes possible to suppress formation of exciton associates leading to thermal deactivation, thus also

reducing quenching process to improve phosphorescence yield and device characteristics.

[0048] In the present invention, as the aromatic substituent for the metal coordination compound of the formula (I), it is preferred to use an aromatic group selected from the group consisting of those (sPh to sPe) shown hereinafter.

[0049] In the present invention, the luminescence device may preferably include the organic layer comprising the above-mentioned metal coordination compound between a pair of oppositely disposed electrodes comprising a transparent electrode (anode) and a metal electrode (cathode) which are supplied with a voltage to cause luminescence, thus constituting an electric-field luminescence device.

[0050] The luminescence device of the present invention has a layer structure shown in Figures 1A to 1C as specifically described above.

[0051] By the use of the metal coordination compound of formula (1) of the present invention, the resultant luminescence device has a high luminescence efficiency as described above.

[0052] The luminescence device according to the present invention may be applicable to devices required to allow energy saving and high luminance, such as those for display apparatus and illumination apparatus, a light source for printers, and backlight (unit) for a liquid crystal display apparatus. Specifically, in the case of using the luminescence device of the present invention in the display apparatus, it is possible to provide a flat panel display apparatus capable of exhibiting an excellent energy saving performance, a high visibility and a good lightweight property. With respect to the light source, it becomes possible to replace a laser light source of laser beam printer currently used widely with the luminescence device according to the present invention. Further, when the luminescence device of the present invention is arranged in independently addressable arrays as an exposure means for effecting desired exposure of light to a photosensitive drum for forming an image, it becomes possible to considerably reducing the volume (size) of image forming apparatus. With respect to the illumination apparatus and backlight (unit), the resultant apparatus (unit) using the luminescence device of the present invention is expected to have an energy saving effect.

[0053] For the application to a display, a drive system using a thin-film transistor (TFT) drive circuit according to an active matrix-scheme may be used. Hereinbelow, an embodiment of using a device of the present invention in combination with an active matrix substrate is briefly described with reference to Figure 2.

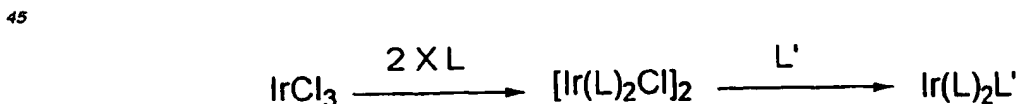
[0054] Figure 2 illustrates an embodiment of panel structure comprising an EL device and drive means. The panel is provided with a scanning signal driver, a data signal driver and a current supply source which are connected to gate selection lines, data signal lines and current supply lines, respectively. At each intersection of the gate selection lines and the data signal lines, a display pixel electrode is disposed. The scanning signal drive sequentially selects the gate selection lines G1, G2, G3 ... Gn, and in synchronism herewith, picture signals are supplied from the data signal driver to display a picture (image).

[0055] By driving a display panel including a luminescence layer comprising a luminescence material of the present invention, it becomes possible to provide a display which exhibits a good picture quality and is stable even for a long period display.

[0056] Some synthetic paths for providing a metal coordination compound represented by the above-mentioned formula (1) are illustrated below with reference to an iridium coordination compound ($m+n=3$) for example:



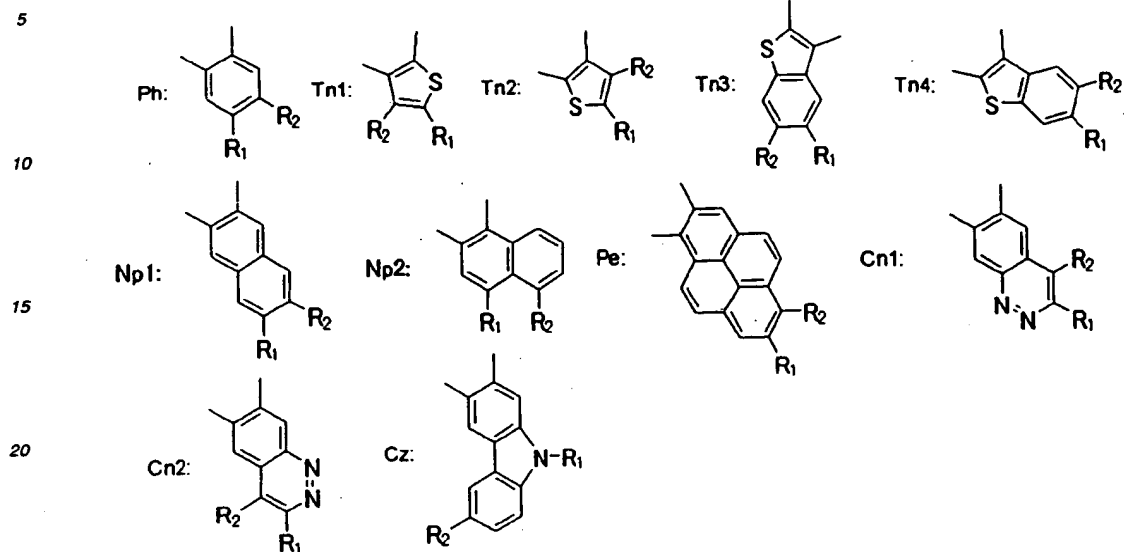
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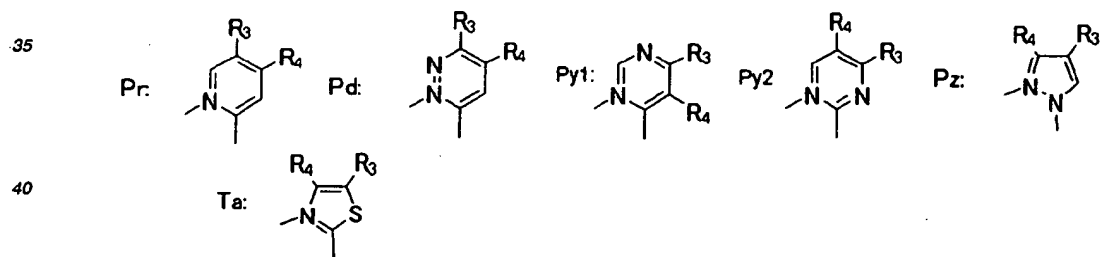
[0057] Other metal coordination compound (M = Pt, Rh and Pd) can also be synthesized in a similar manner.

[0058] Some specific structural examples of metal coordination compounds used in the present invention are shown in Tables 1 to Tables 17 appearing hereinafter, which are however only representative examples and are not exhaustive. Ph to sPe for CyN1, CyN2, CyC1, CyC2 and aromatic substituent(s) shown in Tables 1 to 17 represent partial structures shown below.

<CyC1, CyC2>



<CyN1, CyN2>



<Aromatic substituent>

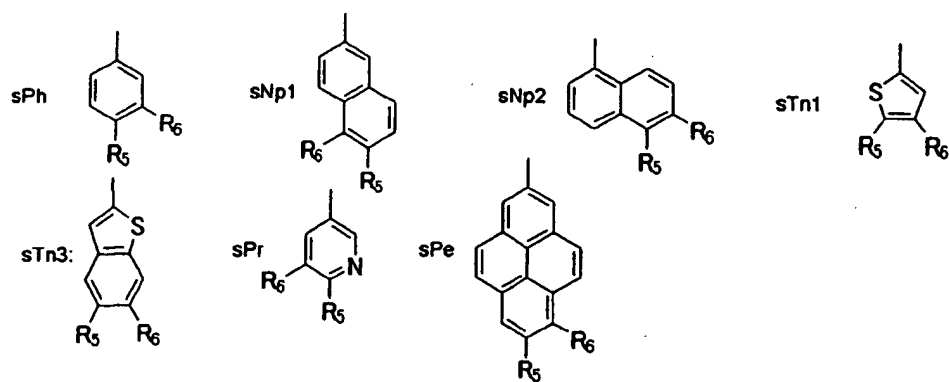


Table 1

No	M	m	CyN1	CyC1	R1	R2	R3	R4
1	Ir	3	Pr	Ph	H	H	sPh	H
2	Ir	3	Pr	Ph	H	H	sNp1	H
3	Ir	3	Pr	Ph	H	H	sNp2	H
4	Ir	3	Pr	Ph	H	H	sTn1	H
5	Ir	3	Pr	Ph	H	H	sTn3	H
6	Ir	3	Pr	Ph	H	H	sPr	H
7	Ir	3	Pr	Ph	H	H	sPe	H
8	Ir	3	Pr	Tn1	H	H	sPh	H
9	Ir	3	Pr	Tn1	H	H	sNp1	H
10	Ir	3	Pr	Tn1	H	H	sNp2	H
11	Ir	3	Pr	Tn1	H	H	sTn1	H
12	Ir	3	Pr	Tn1	H	H	sTn3	H
13	Ir	3	Pr	Tn1	H	H	sPr	H
14	Ir	3	Pr	Tn1	H	H	sPe	H
15	Ir	3	Pr	Tn2	H	H	sPh	H
16	Ir	3	Pr	Tn2	H	H	sNp1	H
17	Ir	3	Pr	Tn2	H	H	sNp2	H
18	Ir	3	Pr	Tn2	H	H	sTn1	H
19	Ir	3	Pr	Tn2	H	H	sTn3	H
20	Ir	3	Pr	Tn2	H	H	sPr	H
21	Ir	3	Pr	Tn2	H	H	sPe	H
22	Ir	3	Pr	Tn3	H	H	sPh	H
23	Ir	3	Pr	Tn3	H	H	sNp1	H

Table 1 (continued)

No	M	m	CyN1	CyC1	R1	R2	R3	R4
24	Ir	3	Pr	Tn3	H	H	sNp2	H
25	Ir	3	Pr	Tn3	H	H	sTn1	H
26	Ir	3	Pr	Tn3	H	H	sTn3	H
27	Ir	3	Pr	Tn3	H	H	sPr	H
28	Ir	3	Pr	Tn3	H	H	sPe	H
29	Ir	3	Pr	Tn4	H	H	sPh	H
30	Ir	3	Pr	Tn4	H	H	sNp1	H
31	Ir	3	Pr	Tn4	H	H	sNp2	H
32	Ir	3	Pr	Tn4	H	H	sTn1	H
33	Ir	3	Pr	Tn4	H	H	sTn3	H
34	Ir	3	Pr	Tn4	H	H	sPr	H
35	Ir	3	Pr	Tn4	H	H	sPe	H
36	Ir	3	Pr	Np1	H	H	sPh	H
37	Ir	3	Pr	Np1	H	H	sNp1	H
38	Ir	3	Pr	Np1	H	H	sNp2	H
39	Ir	3	Pr	Np1	H	H	sTn1	H
40	Ir	3	Pr	Np1	H	H	sTn3	H
41	Ir	3	Pr	Np1	H	H	sPr	H
42	Ir	3	Pr	Np1	H	H	sPe	H
43	Ir	3	Pr	Np2	H	H	H	sPh
44	Ir	3	Pr	Np2	H	H	sNp1	H
45	Ir	3	Pr	Np2	H	H	sNp2	H
46	Ir	3	Pr	Np2	H	H	sTn1	H
47	Ir	3	Pr	Np2	H	H	sTn3	H
48	Ir	3	Pr	Np2	H	H	sPr	H
49	Ir	3	Pr	Np2	H	H	sPe	H
50	Ir	3	Pr	Pe	H	H	sPh	H
51	Ir	3	Pr	Pe	H	H	sNp1	H
52	Ir	3	Pr	Pe	H	H	sNp2	H

Table 2

No	M	m	CyN1	CyC1	R1	R2	R3	R4
53	Ir	3	Pr	Pe	H	H	sTn1	H
54	Ir	3	Pr	Pe	H	H	sTn3	H
55	Ir	3	Pr	Pe	H	H	sPr	H
56	Ir	3	Pr	Pe	H	H	sPe	H
57	Ir	3	Pr	Cn1	H	H	sPh	H
58	Ir	3	Pr	Cn1	H	H	sNp1	H

Table 2 (continued)

No	M	m	CyN1	CyC1	R1	R2	R3	R4
59	Ir	3	Pr	Cn1	H	H	sNp2	H
60	Ir	3	Pr	Cn1	H	H	sTn1	H
61	Ir	3	Pr	Cn1	H	H	sTn3	H
62	Ir	3	Pr	Cn1	H	H	sPr	H
63	Ir	3	Pr	Cn1	H	H	sPe	H
64	Ir	3	Pr	Cn2	H	H	sPh	H
65	Ir	3	Pr	Cn2	H	H	sNp1	H
66	Ir	3	Pr	Cn2	H	H	sNp2	H
67	Ir	3	Pr	Cn2	H	H	sTn1	H
68	Ir	3	Pr	Cn2	H	H	sTn3	H
69	Ir	3	Pr	Cn2	H	H	sPr	H
70	Ir	3	Pr	Cn2	H	H	sPe	H
71	Ir	3	Pr	Cz	H	H	sPh	H
72	Ir	3	Pr	Cz	H	H	sNp1	H
73	Ir	3	Pr	Cz	H	H	sNp2	H
74	Ir	3	Pr	Cz	H	H	sTn1	H
75	Ir	3	Pr	Cz	H	H	sTn3	H
76	Ir	3	Pr	Cz	H	H	sPr	H
77	Ir	3	Pr	Cz	H	H	sPe	H
78	Ir	3	Pd	Ph	H	H	sPh	H
79	Ir	3	Pd	Ph	H	H	sNp1	H
80	Ir	3	Pd	Ph	H	H	sNp2	H
81	Ir	3	Pd	Ph	H	H	sTn1	H
82	Ir	3	Pd	Ph	H	H	sTn3	H
83	Ir	3	Pd	Ph	H	H	sPr	H
84	Ir	3	Pd	Ph	H	H	sPe	H
85	Ir	3	Pd	Tn1	H	H	sPh	H
86	Ir	3	Pd	Tn1	H	H	sNp1	H
87	Ir	3	Pd	Tn1	H	H	sNp2	H
88	Ir	3	Pd	Tn1	H	H	sTn1	H
89	Ir	3	Pd	Tn1	H	H	sTn3	H
90	Ir	3	Pd	Tn1	H	H	sPr	H
91	Ir	3	Pd	Tn1	H	H	sPe	H
92	Ir	3	Pd	Tn2	H	H	sPh	H
93	Ir	3	Pd	Tn2	H	H	sNp1	H
94	Ir	3	Pd	Tn2	H	H	sNp2	H
95	Ir	3	Pd	Tn2	H	H	sTn1	H
96	Ir	3	Pd	Tn2	H	H	sTn3	H

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Table 2 (continued)

No	M	m	CyN1	CyC1	R1	R2	R3	R4
97	Ir	3	Pd	Tn2	H	H	sPr	H
98	Ir	3	Pd	Tn2	H	H	sPe	H
99	Ir	3	Pd	Tn3	H	H	sPh	H
100	Ir	3	Pd	Tn3	H	H	sNp1	H
101	Ir	3	Pd	Tn3	H	H	sNp2	H
102	Ir	3	Pd	Tn3	H	H	sTn1	H
103	Ir	3	Pd	Tn3	H	H	sTn3	H
104	Ir	3	Pd	Tn3	H	H	sPr	H

Table 3

No	M	m	CyN1	CyC1	R1	R2	R3	R4
105	Ir	3	Pd	Tn3	H	H	sPe	H
106	Ir	3	Pd	Tn4	H	H	sPh	H
107	Ir	3	Pd	Tn4	H	H	sNp1	H
108	Ir	3	Pd	Tn4	H	H	sNp2	H
109	Ir	3	Pd	Tn4	H	H	sTn1	H
110	Ir	3	Pd	Tn4	H	H	sTn3	H
111	Ir	3	Pd	Tn4	H	H	sPr	H
112	Ir	3	Pd	Tn4	H	H	sPe	H
113	Ir	3	Pd	Np1	H	H	sPh	H
114	Ir	3	Pd	Np1	H	H	sNp1	H
115	Ir	3	Pd	Np1	H	H	sNp2	H
116	Ir	3	Pd	Np1	H	H	sTn1	H
117	Ir	3	Pd	Np1	H	H	sTn3	H
118	Ir	3	Pd	Np1	H	H	sPr	H
119	Ir	3	Pd	Np1	H	H	sPe	H
120	Ir	3	Pd	Np2	H	H	sPh	H
121	Ir	3	Pd	Np2	H	H	sNp1	H
122	Ir	3	Pd	Np2	H	H	sNp2	H
123	Ir	3	Pd	Np2	H	H	sTn1	H
124	Ir	3	Pd	Np2	H	H	sTn3	H
125	Ir	3	Pd	Np2	H	H	sPr	H
126	Ir	3	Pd	Np2	H	H	sPe	H
127	Ir	3	Pd	Pe	H	H	sPh	H
128	Ir	3	Pd	Pe	H	H	sNp1	H
129	Ir	3	Pd	Pe	H	H	sNp2	H
130	Ir	3	Pd	Pe	H	H	sTn1	H
131	Ir	3	Pd	Pe	H	H	sTn3	H

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Table 3 (continued)

No	M	m	CyN1	CyC1	R1	R2	R3	R4
132	Ir	3	Pd	Pe	H	H	sPr	H
133	Ir	3	Pd	Pe	H	H	sPe	H
134	Ir	3	Pd	Cn1	H	H	sPh	H
135	Ir	3	Pd	Cn1	H	H	sNp1	H
136	Ir	3	Pd	Cn1	H	H	sNp2	H
137	Ir	3	Pd	Cn1	H	H	sTn1	H
138	Ir	3	Pd	Cn1	H	H	sTn3	H
139	Ir	3	Pd	Cn1	H	H	sPr	H
140	Ir	3	Pd	Cn1	H	H	sPe	H
141	Ir	3	Pd	Cn2	H	H	sPh	H
142	Ir	3	Pd	Cn2	H	H	sNp1	H
143	Ir	3	Pd	Cn2	H	H	sNp2	H
144	Ir	3	Pd	Cn2	H	H	sTn1	H
145	Ir	3	Pd	Cn2	H	H	sTn3	H
146	Ir	3	Pd	Cn2	H	H	sPr	H
147	Ir	3	Pd	Cn2	H	H	sPe	H
148	Ir	3	Pd	Cz	H	H	sPh	H
149	Ir	3	Pd	Cz	H	H	sNp1	H
150	Ir	3	Pd	Cz	H	H	sNp2	H
151	Ir	3	Pd	Cz	H	H	sTn1	H
152	Ir	3	Pd	Cz	H	H	sTn3	H
153	Ir	3	Pd	Cz	H	H	sPr	H
154	Ir	3	Pd	Cz	H	H	sPe	H
155	Ir	3	Pz	Ph	H	H	sPh	H
156	Ir	3	Pd	Ph	H	H	sNp1	H

Table 4

No	M	m	CyN1	CyC1	R1	R2	R3	R4
157	Ir	3	Pd	Ph	H	H	sNp2	H
158	Ir	3	Pd	Ph	H	H	sTn1	H
159	Ir	3	Pd	Ph	H	H	sTn3	H
160	Ir	3	Pd	Ph	H	H	sPr	H
161	Ir	3	Pd	Ph	H	H	sPe	H
162	Ir	3	Pd	Tn1	H	H	sPh	H
163	Ir	3	Pd	Tn1	H	H	sNp1	H
164	Ir	3	Pd	Tn1	H	H	sNp2	H
165	Ir	3	Pd	Tn1	H	H	sTn1	H
166	Ir	3	Pd	Tn1	H	H	sTn3	H

Table 4 (continued)

No	M	m	CyN1	CyC1	R1	R2	R3	R4
167	Ir	3	Pd	Tn1	H	H	sPr	H
168	Ir	3	Pd	Tn1	H	H	sPe	H
169	Ir	3	Pd	Tn2	H	H	sPh	H
170	Ir	3	Pd	Tn2	H	H	sNp1	H
171	Ir	3	Pd	Tn2	H	H	sNp2	H
172	Ir	3	Pd	Tn2	H	H	sTn1	H
173	Ir	3	Pd	Tn2	H	H	sTn3	H
174	Ir	3	Pd	Tn2	H	H	sPr	H
175	Ir	3	Pd	Tn2	H	H	sPe	H
176	Ir	3	Pd	Tn3	H	H	sPh	H
177	Ir	3	Pd	Tn3	H	H	sNp1	H
178	Ir	3	Pd	Tn3	H	H	sNp2	H
179	Ir	3	Pd	Tn3	H	H	sTn1	H
180	Ir	3	Pd	Tn3	H	H	sTn3	H
181	Ir	3	Pd	Tn3	H	H	sPr	H
182	Ir	3	Pd	Tn3	H	H	sPe	H
183	Ir	3	Pd	Tn4	H	H	sPh	H
184	Ir	3	Pd	Tn4	H	H	sNp1	H
185	Ir	3	Pd	Tn4	H	H	sNp2	H
186	Ir	3	Pd	Tn4	H	H	sTn1	H
187	Ir	3	Pd	Tn4	H	H	sTn3	H
188	Ir	3	Pd	Tn4	H	H	sPr	H
189	Ir	3	Pd	Tn4	H	H	sPe	H
190	Ir	3	Pd	Np1	H	H	sPh	H
191	Ir	3	Pd	Np1	H	H	sNp1	H
192	Ir	3	Pd	Np1	H	H	sNp2	H
193	Ir	3	Pd	Np1	H	H	sTn1	H
194	Ir	3	Pd	Np1	H	H	sTn3	H
195	Ir	3	Pd	Np1	H	H	sPr	H
196	Ir	3	Pd	Np1	H	H	sPe	H
197	Ir	3	Pd	Np2	H	H	sPh	H
198	Ir	3	Pd	Np2	H	H	sNp1	H
199	Ir	3	Pd	Np2	H	H	sNp2	H
200	Ir	3	Pd	Np2	H	H	sTn1	H
201	Ir	3	Pd	Np2	H	H	sTn3	H
202	Ir	3	Pd	Np2	H	H	sPr	H
203	Ir	3	Pd	Np2	H	H	sPe	H
204	Ir	3	Pd	Pe	H	H	sPh	H

Table 4 (continued)

No	M	m	CyN1	CyC1	R1	R2	R3	R4
205	Ir	3	Pd	Pe	H	H	sNp1	H
206	Ir	3	Pd	Pe	H	H	sNp2	H
207	Ir	3	Pd	Pe	H	H	sTn1	H
208	Ir	3	Pd	Pe	H	H	sTn3	H

Table 5

No	M	m	CyN1	CyC1	R1	R2	R3	R4
209	Ir	3	Pd	Pe	H	H	sPr	H
210	Ir	3	Pd	Pe	H	H	sPe	H
211	Ir	3	Pd	Cn1	H	H	sPh	H
212	Ir	3	Pd	Cn1	H	H	sNp1	H
213	Ir	3	Pd	Cn1	H	H	sNp2	H
214	Ir	3	Pd	Cn1	H	H	sTn1	H
215	Ir	3	Pd	Cn1	H	H	sTn3	H
216	Ir	3	Pd	Cn1	H	H	sPr	H
217	Ir	3	Pd	Cn1	H	H	sPe	H
218	Ir	3	Pd	Cn2	H	H	sPh	H
219	Ir	3	Pd	Cn2	H	H	sNp1	H
220	Ir	3	Pd	Cn2	H	H	sNp2	H
221	Ir	3	Pd	Cn2	H	H	sTn1	H
222	Ir	3	Pd	Cn2	H	H	sTn3	H
223	Ir	3	Pd	Cn2	H	H	sPr	H
224	Ir	3	Pd	Cn2	H	H	sPe	H
225	Ir	3	Pd	Cz	H	H	sPh	H
226	Ir	3	Pd	Cz	H	H	sNp1	H
227	Ir	3	Pd	Cz	H	H	sNp2	H
228	Ir	3	Pd	Cz	H	H	sTn1	H
229	Ir	3	Pd	Cz	H	H	sTn3	H
230	Ir	3	Pd	Cz	H	H	sPr	H
231	Ir	3	Pd	Cz	H	H	sPe	H
232	Ir	3	Pz	Ph	H	H	sPh	H
233	Ir	3	Pz	Ph	H	H	sNp1	H
234	Ir	3	Pz	Ph	H	H	sNp2	H
235	Ir	3	Pz	Ph	H	H	sTn1	H
236	Ir	3	Pz	Ph	H	H	sTn3	H
237	Ir	3	Pz	Ph	H	H	sPr	H
238	Ir	3	Pz	Ph	H	H	sPe	H
239	Ir	3	Pz	Tn1	H	H	sPh	H

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Table 5 (continued)

No	M	m	CyN1	CyC1	R1	R2	R3	R4
240	Ir	3	Pz	Tn1	H	H	sNp1	H
241	Ir	3	Pz	Tn1	H	H	sNp2	H
242	Ir	3	Pz	Tn1	H	H	sTn1	H
243	Ir	3	Pz	Tn1	H	H	sTn3	H
244	Ir	3	Pz	Tn1	H	H	sPr	H
245	Ir	3	Pz	Tn1	H	H	sPe	H
246	Ir	3	Pz	Tn2	H	H	sPh	H
247	Ir	3	Pz	Tn2	H	H	sNp1	H
248	Ir	3	Pz	Tn2	H	H	sNp2	H
249	Ir	3	Pz	Tn2	H	H	sTn1	H
250	Ir	3	Pz	Tn2	H	H	sTn3	H
251	Ir	3	Pz	Tn2	H	H	sPr	H
252	Ir	3	Pz	Tn2	H	H	sPe	H
253	Ir	3	Pz	Tn3	H	H	sPh	H
254	Ir	3	Pz	Tn3	H	H	sNp1	H
255	Ir	3	Pz	Tn3	H	H	sNp2	H
256	Ir	3	Pz	Tn3	H	H	sTn1	H
257	Ir	3	Pz	Tn3	H	H	sTn3	H
258	Ir	3	Pz	Tn3	H	H	sPr	H
259	Ir	3	Pz	Tn3	H	H	sPe	H
260	Ir	3	Pz	Tn4	H	H	sPh	H

Table 6

No	M	m	CyN1	CyC1	R1	R2	R3	R4
261	Ir	3	Pz	Tn4	H	H	sNp1	H
262	Ir	3	Pz	Tn4	H	H	sNp2	H
263	Ir	3	Pz	Tn4	H	H	sTn1	H
264	Ir	3	Pz	Tn4	H	H	sTn3	H
265	Ir	3	Pz	Tn4	H	H	sPr	H
266	Ir	3	Pz	Tn4	H	H	sPe	H
267	Ir	3	Pz	Np1	H	H	sPh	H
268	Ir	3	Pz	Np1	H	H	sNp1	H
269	Ir	3	Pz	Np1	H	H	sNp2	H
270	Ir	3	Pz	Np1	H	H	sTn1	H
271	Ir	3	Pz	Np1	H	H	sTn3	H
272	Ir	3	Pz	Np1	H	H	sPr	H
273	Ir	3	Pz	Np1	H	H	sPe	H
274	Ir	3	Pz	Np2	H	H	sPh	H

Table 6 (continued)

No	M	m	CyN1	CyC1	R1	R2	R3	R4
275	Ir	3	Pz	Np2	H	H	sNp1	H
276	Ir	3	Pz	Np2	H	H	sNp2	H
277	Ir	3	Pz	Np2	H	H	sTn1	H
278	Ir	3	Pz	Np2	H	H	sTn3	H
279	Ir	3	Pz	Np2	H	H	sPr	H
280	Ir	3	Pz	Np2	H	H	sPe	H
281	Ir	3	Pz	Pe	H	H	sPh	H
282	Ir	3	Pz	Pe	H	H	sNp1	H
283	Ir	3	Pz	Pe	H	H	sNp2	H
284	Ir	3	Pz	Pe	H	H	sTn1	H
285	Ir	3	Pz	Pe	H	H	sTn3	H
286	Ir	3	Pz	Pe	H	H	sPr	H
287	Ir	3	Pz	Pe	H	H	sPe	H
288	Ir	3	Pz	Cn1	H	H	sPh	H
289	Ir	3	Pz	Cn1	H	H	sNp1	H
290	Ir	3	Pz	Cn1	H	H	sNp2	H
291	Ir	3	Pz	Cn1	H	H	sTn1	H
292	Ir	3	Pz	Cn1	H	H	sTn3	H
293	Ir	3	Pz	Cn1	H	H	sPr	H
294	Ir	3	Pz	Cn1	H	H	sPe	H
295	Ir	3	Pz	Cn2	H	H	sPh	H
296	Ir	3	Pz	Cn2	H	H	sNp1	H
297	Ir	3	Pz	Cn2	H	H	sNp2	H
298	Ir	3	Pz	Cn2	H	H	sTn1	H
299	Ir	3	Pz	Cn2	H	H	sTn3	H
300	Ir	3	Pz	Cn2	H	H	sPr	H
301	Ir	3	Pz	Cn2	H	H	sPe	H
302	Ir	3	Pz	Cz	H	H	sPh	H
303	Ir	3	Pz	Cz	H	H	sNp1	H
304	Ir	3	Pz	Cz	H	H	sNp2	H
305	Ir	3	Pz	Cz	H	H	sTn1	H
306	Ir	3	Pz	Cz	H	H	sTn3	H
307	Ir	3	Pz	Cz	H	H	sPr	H
308	Ir	3	Pz	Cz	H	H	sPe	H
309	Ir	3	Py1	Ph	H	H	sPh	H
310	Ir	3	Py1	Ph	H	H	sNp1	H
311	Ir	3	Py1	Ph	H	H	sTn1	H
312	Ir	3	Py1	Ph	H	H	sTn3	H

Table 7

No	M	m	CyN1	CyC1	R1	R2	R3	R4
313	Ir	3	Py1	Tn1	H	H	sPh	H
314	Ir	3	Py1	Tn1	H	H	sNp1	H
315	Ir	3	Py1	Tn1	H	H	sTn1	H
316	Ir	3	Py1	Tn1	H	H	sTn3	H
317	Ir	3	Py1	Tn3	H	H	sPh	H
318	Ir	3	Py1	Tn3	H	H	sNp1	H
319	Ir	3	Py1	Tn3	H	H	sTn1	H
320	Ir	3	Py1	Tn3	H	H	sTn3	H
321	Ir	3	Py1	Tn4	H	H	sPh	H
322	Ir	3	Py1	Tn4	H	H	sNp1	H
323	Ir	3	Py1	Tn4	H	H	sTn1	H
324	Ir	3	Py1	Tn4	H	H	sTn3	H
325	Ir	3	Py1	Np2	H	H	sPh	H
326	Ir	3	Py1	Np2	H	H	sNp1	H
327	Ir	3	Py1	Np2	H	H	sTn1	H
328	Ir	3	Py1	Np2	H	H	sTn3	H
329	Ir	3	Py2	Ph	H	H	sPh	H
330	Ir	3	Py2	Ph	H	H	sNp1	H
331	Ir	3	Py2	Ph	H	H	sTn1	H
332	Ir	3	Py2	Ph	H	H	sTn3	H
333	Ir	3	Py2	Tn1	H	H	sPh	H
334	Ir	3	Py2	Tn1	H	H	sNp1	H
335	Ir	3	Py2	Tn1	H	H	sTn1	H
336	Ir	3	Py2	Tn1	H	H	sTn3	H
337	Ir	3	Py2	Tn3	H	H	sPh	H
338	Ir	3	Py2	Tn3	H	H	sNp1	H
339	Ir	3	Py2	Tn3	H	H	sTn1	H
340	Ir	3	Py2	Tn3	H	H	sTn3	H
341	Ir	3	Py2	Tn4	H	H	sPh	H
342	Ir	3	Py2	Tn4	H	H	sNp1	H
343	Ir	3	Py2	Tn4	H	H	sTn1	H
344	Ir	3	Py2	Tn4	H	H	sTn3	H
345	Ir	3	Py2	Np2	H	H	sPh	H
346	Ir	3	Py2	Np2	H	H	sNp1	H
347	Ir	3	Py2	Np2	H	H	sTn1	H
348	Ir	3	Py2	Np2	H	H	sTn3	H
349	Ir	3	Pr	Ph	sPh	H	H	H

Table 7 (continued)

No	M	m	CyN1	CyC1	R1	R2	R3	R4
350	Ir	3	Pr	Ph	sNp2	H	H	H
351	Ir	3	Pr	Ph	sTn1	H	H	H
352	Ir	3	Pr	Ph	sTn3	H	H	H
353	Ir	3	Pr	Tn1	sPh	H	H	H
354	Ir	3	Pr	Tn1	sNp2	H	H	H
355	Ir	3	Pr	Tn1	sTn1	H	H	H
356	Ir	3	Pr	Tn1	sTn3	H	H	H
357	Ir	3	Pr	Tn3	sPh	H	H	H
358	Ir	3	Pr	Tn3	sNp2	H	H	H
359	Ir	3	Pr	Tn3	sTn1	H	H	H
360	Ir	3	Pr	Tn3	sTn3	H	H	H
361	Ir	3	Pr	Np2	sPh	H	H	H
362	Ir	3	Pr	Np2	sNp2	H	H	H
363	Ir	3	Pr	Np2	sTn1	H	H	H
364	Ir	3	Pr	Np2	sTn3	H	H	H

Table 8

No	M	m	CyN1	CyC1	R1	R2	R3	R4
365	Ir	3	Pz	Ph	sPh	H	H	H
366	Ir	3	Pz	Ph	sNp2	H	H	H
367	Ir	3	Pz	Ph	sTn1	H	H	H
368	Ir	3	Pz	Ph	sTn3	H	H	H
369	Ir	3	Pz	Tn1	sPh	H	H	H
370	Ir	3	Pz	Tn1	sNp2	H	H	H
371	Ir	3	Pz	Tn1	sTn1	H	H	H
372	Ir	3	Pz	Tn1	sTn3	H	H	H
373	Ir	3	Pz	Tn3	sPh	H	H	H
374	Ir	3	Pz	Tn3	sNp2	H	H	H
375	Ir	3	Pz	Tn3	sTn1	H	H	H
376	Ir	3	Pz	Tn3	sTn3	H	H	H
377	Ir	3	Pz	Np2	sPh	H	H	H
378	Ir	3	Pz	Np2	sNp2	H	H	H
379	Ir	3	Pz	Np2	sTn1	H	H	H
380	Ir	3	Pz	Np2	sTn3	H	H	H

Table 9

No	M	m	CyN1	CyC1	R1	R2	R3	R4	R5	R6
381	Ir	3	Pr	Ph	sPh	H	H	H	H	-NO2

Table 9 (continued)

No	M	m	CyN1	CyC1	R1	R2	R3	R4	R5	R6
382	Ir	3	Pr	Ph	sNp2	H	-CH3	H	H	H
383	Ir	3	Pr	Ph	sTn1	H	H	H	-CF3	H
384	Ir	3	Pr	Ph	sTn3	H	H	H	H	sPh
385	Ir	3	Pr	Tn1	sPh	H	H	H	-OCH ₃	H
386	Ir	3	Pr	Tn1	sNp2	H	H	H	H	sPh
387	Ir	3	Pr	Tn1	sTn1	H	H	H	H	-CF3
388	Ir	3	Pr	Tn1	sTn3	H	H	H	H	sPh
389	Ir	3	Pr	Tn3	sPh	H	H	H	-OCH ₃	H
390	Ir	3	Pr	Tn3	sNp2	H	H	H	H	-OCH ₃
391	Ir	3	Pr	Tn3	sTn1	H	H	H	H	-OCH ₃
392	Ir	3	Pr	Tn3	sTn3	H	H	H	-OCH ₃	H
393	Ir	3	Pr	Np2	sPh	H	H	H	-OCH ₃	H
394	Ir	3	Pr	Np2	sNp2	H	H	H	H	sPh
395	Ir	3	Pr	Np2	sTn1	H	H	H	H	sPh
396	Ir	3	Pr	Np2	sTn3	H	H	H	H	-OCH ₃
397	Ir	3	Pz	Ph	sPh	H	H	-OCH ₃	H	H
398	Ir	3	Pz	Ph	sNp2	H	H	-OCH ₃	H	H
399	Ir	3	Pz	Ph	sTn1	H	H	H	H	-OCH ₃
400	Ir	3	Pz	Ph	sTn3	H	H	H	H	-OCH ₃
401	Ir	3	Pz	Tn1	sPh	H	-C3H7	H	H	H
402	Ir	3	Pz	Tn1	sNp2	H	H	H	H	H
403	Ir	3	Pz	Tn1	sTn1	H	H	H	H	H
404	Ir	3	Pz	Tn1	sTn3	H	H	H	H	sPh
405	Ir	3	Pz	Tn3	sPh	H	H	H	H	-OCH ₃
406	Ir	3	Pz	Tn3	sNp2	H	H	-OCH ₃	H	H
407	Ir	3	Pz	Tn3	sTn1	H	H	-OCH ₃	H	H
408	Ir	3	Pz	Tn3	sTn3	H	H	H	H	-OCH ₃
409	Ir	3	Pz	Np2	sPh	H	H	H	H	-OCH ₃
410	Ir	3	Pz	Np2	sNp2	H	-C3H7	H	H	H

Table 10

No	M	m	CyN1	CyC1	R1	R2	R3	R4	R5	R6
411	Ir	3	Pz	Np2	sTn1	H	H	-CF3	H	H
412	Ir	3	Pz	Np2	sTn3	H	H	-CF3	H	H
413	Ir	3	Ta	Ph	C4H9	C4H9	sPh	H	OCH3	H
414	Ir	3	Pr	Ph	sPh	H	H	H	H	H
415	Ir	3	Pr	Ph	sNp2	H	-CH3	H	H	H
416	Ir	3	Pr	Ph	sTn1	H	H	H	H	H

Table 10 (continued)

No	M	m	CyN1	CyC1	R1	R2	R3	R4	R5	R6
417	Ir	3	Pr	Ph	sTn3	H	H	H	H	H
418	Ir	3	Pr	Tn1	sPh	H	H	H	-OCH ₃	H
419	Ir	3	Pr	Tn1	sNp2	H	H	H	H	H
420	Ir	3	Pr	Tn1	sTn1	H	H	H	H	H
421	Ir	3	Pr	Tn1	sTn3	H	H	H	H	H
422	Ir	3	Pr	Tn3	sPh	H	H	H	-OCH ₃	H
423	Ir	3	Pr	Tn3	sNp2	H	H	H	H	H
424	Ir	3	Pr	Tn3	sTn1	H	-NO ₂	H	H	H
425	Ir	3	Pr	Tn3	sTn3	H	H	H	H	H
426	Ir	3	Pr	Np2	sPh	H	H	H	H	H
427	Ir	3	Pr	Np2	sNp2	H	H	H	H	H
428	Ir	3	Pr	Np2	sTn1	H	H	H	H	H
429	Ir	3	Pr	Np2	sTn3	H	H	H	H	H
430	Ir	3	Pz	Ph	sPh	H	H	-F	H	H
431	Ir	3	Pz	Ph	sNp2	H	H	H	H	H
432	Ir	3	Pz	Ph	sTn1	-CN	H	H	H	H
433	Ir	3	Pz	Ph	sTn3	H	H	H	H	H
434	Ir	3	Pz	Tn1	sPh	H	-C3H7	H	H	H
435	Ir	3	Pz	Tn1	sNp2	H	H	-CH ₂ -CH=CH-CH ₃	H	H
436	Ir	3	Pz	Tn1	sTn1	H	H	H	H	H
437	Ir	3	Pz	Tn1	sTn3	H	H	H	H	H
438	Ir	3	Pz	Tn3	sPh	H	-SC3H7	H	H	H
439	Ir	3	Pz	Tn3	sNp2	H	H	H	H	H
440	Ir	3	Pz	Tn3	sTn1	H	H	H	H	H
441	Ir	3	Pz	Tn3	sTn3	H	H		H	H
442	Ir	3	Pz	Np2	sPh	H	H	H	H	H
443	Ir	3	Pz	Np2	sNp2	H	H	H	H	H
444	Ir	3	Pz	Np2	sTn1	H	H	H	H	H
445	Ir	3	Pz	Np2	sTn3	H	H	H	H	H

Table 11

No	M	m	n	CyN1	CyC1	CyN2	CyC2	R1	R2	R3	R4	R1'	R2'	R3'	R4'
446	Ir	2	1	Pr	Ph	Pr	Tn1	sPh	H	H	H	sPh	H	H	H
447	Ir	2	1	Pr	Ph	Pr	Tn1	sNp2	H	H	H	sNp2	H	H	H
448	Ir	2	1	Pr	Ph	Pr	Tn1	sTn1	H	H	H	sTn1	H	H	H
449	Ir	2	1	Pr	Ph	Pr	Tn1	sTn3	H	H	H	sTn3	H	H	H
450	Ir	2	1	Pr	Tn3	Pr	Np2	sPh	H	H	H	sPh	H	H	H
451	Ir	2	1	Pr	Tn3	Pr	Np2	sNp2	H	H	H	sNp2	H	H	H

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Table 11 (continued)

No	M	m	n	CyN1	CyC1	CyN2	CyC2	R1	R2	R3	R4	R1'	R2'	R3'	R4'
452	Ir	2	1	Pr	Tn3	Pr	Np2	sTn1	H	H	H	sTn1	H	H	H
453	Ir	2	1	Pr	Tn3	Pr	Np2	sTn3	H	H	H	sTn3	H	H	H

Table 12

No	M	m	n	CyN1	CyC1	E	G	R1	R2	R3	R4
454	Ir	Ir	1	Pr	Ph	-CH3	-CH3	sPh	H	H	H
455	Ir	Ir	1	Pr	Ph	-CH3	-CH3	sNp2	H	H	H
456	Ir	Ir	1	Pr	Ph	-CH3	-CH3	sTn1	H	H	H
457	Ir	Ir	1	Pr	Ph	-CH3	-CH3	H	H	sTn3	H
458	Ir	Ir	1	Pr	Tn3	-CH3	sPh	H	H	sPh	H
459	Ir	Ir	1	Pr	Tn3	-CH3	sPh	H	H	sNp2	H
460	Ir	Ir	1	Pr	Tn3	-CH3	sPh	H	H	sTn1	H
461	Ir	Ir	1	Pr	Tn3	-CH3	sPh	H	H	sTn3	H

Table 13

No	M	m	CyN1	CyC1	R1	R2	R3	R4
462	Rh	3	Pr	Ph	sPh	H	H	H
463	Rh	3	Pr	Ph	sNp2	H	H	H
464	Rh	3	Pr	Ph	sTn1	H	H	H
465	Rh	3	Pr	Ph	sTn3	H	H	H
466	Rh	3	Pr	Tn1	sPh	H	H	H
467	Rh	3	Pr	Tn1	sNp2	H	H	H
468	Rh	3	Pr	Tn1	sTn1	H	H	H
469	Rh	3	Pr	Tn1	sTn3	H	H	H
470	Rh	3	Pr	Tn3	sPh	H	H	H
471	Rh	3	Pr	Tn3	sNp2	H	H	H
472	Rh	3	Pr	Tn3	sTn1	H	H	H
473	Rh	3	Pr	Tn3	sTn3	H	H	H
474	Rh	3	Pr	Np2	sPh	H	H	H
475	Rh	3	Pr	Np2	sNp2	H	H	H
476	Rh	3	Pr	Np2	sTn1	H	H	H
477	Rh	3	Pr	Np2	sTn3	H	H	H

Table 14

No	M	m	CyN1	CyC1	R1	R2	R3	R4
478	Pt	2	Pr	Ph	sPh	H	H	H
479	Pt	2	Pr	Ph	sNp2	H	H	H

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Table 14 (continued)

No	M	m	CyN1	CyC1	R1	R2	R3	R4
480	Pt	2	Pr	Ph	sTn1	H	H	H
481	Pt	2	Pr	Ph	sTn3	H	H	H
482	Pt	2	Pr	Tn1	sPh	H	H	H
483	Pt	2	Pr	Tn1	sNp2	H	H	H
484	Pt	2	Pr	Tn1	sTn1	H	H	H
485	Pt	2	Pr	Tn1	sTn3	H	H	H
486	Pt	2	Pr	Tn3	sPh	H	H	H
487	Pt	2	Pr	Tn3	sNp2	H	H	H
488	Pt	2	Pr	Tn3	sTn1	H	H	H
489	Pt	2	Pr	Tn3	sTn3	H	H	H
490	Pt	2	Pr	Np2	sPh	H	H	H
491	Pt	2	Pr	Np2	sNp2	H	H	H
492	Pt	2	Pr	Np2	sTn1	H	H	H
493	Pt	2	Pr	Np2	sTn3	H	H	H

Table 15

No	M	m	CyN1	CyC1	R1	R2	R3	R4
494	Pd	2	Pr	Ph	sPh	H	H	H
495	Pd	2	Pr	Ph	sNp2	H	H	H
496	Pd	2	Pr	Ph	sTn1	H	H	H
497	Pd	2	Pr	Ph	sTn3	H	H	H
498	Pd	2	Pr	Tn1	sPh	H	H	H
499	Pd	2	Pr	Tn1	sNp2	H	H	H
500	Pd	2	Pr	Tn1	sTn1	H	H	H
501	Pd	2	Pr	Tn1	sTn3	H	H	H
502	Pd	2	Pr	Tn3	sPh	H	H	H
503	Pd	2	Pr	Tn3	sNp2	H	H	H
504	Pd	2	Pr	Tn3	sTn1	H	H	H
505	Pd	2	Pr	Tn3	sTn3	H	H	H
506	Pd	2	Pr	Np2	sPh	H	H	H
507	Pd	2	Pr	Np2	sNp2	H	H	H
508	Pd	2	Pr	Np2	sTn1	H	H	H
509	Pd	2	Pr	Np2	sTn3	H	H	H

Table 16




No	M	m	CyN1	CyC1	R1	R2	R3	R4	R5	R6
510	Ir	3	Pr	Ph	sPe	H	H	H	H	H
511	Ir	3	Pr	Ph	sPh	H	sPh	H		H
512	Ir	3	Pr	Ph	H		sPh	H	H	
513	Ir	3	Pr	Np2	sPe	H	H	H	H	H
514	Ir	3	Pr	Np2	H	H	sTn1	H	CH3	H
515	Ir	3	Pr	Tn1	CH3	H	sTn1	H	CH3	H
516	Ir	3	Pr	Tn1	sPh	H	sTn1	H	sPh	H

Table 17

No	M	m	n	CyN1	CyC1	R1	R2	R3	R4	E	G
517	Ir	2	1	Pr	Tn3	H	H	sPh	H	CH3	CH3
518	Ir	2	1	Pr	Tn1	H	H	sTn1	H	CH3	CH3
519	Ir	2	1	Pr	Np2	H	H	sNp2	H	CH3	CH3
520	Ir	3	0	Py1	Ph	sPh	H	H	H	-	-
521	Ir	3	0	Py1	Ph	sNp1	H	H	H	-	-
522	Ir	3	0	Pr	Ph	H	H	H	sPh	-	-
523	Ir	3	0	Pr	Ph	H	sPh	H	H	-	-
524	Ir	3	0	Pr	Tn1	Ph	H	H	H	-	-
525	Ir	2	1	Py1	Ph	sPh	H	H	H	CH3	CH3
526	Ir	2	1	Py1	Ph	sNp1	H	H	H	CH3	CH3
527	Ir	2	1	Pr	Ph	H	H	H	sPh	CH3	CH3
528	Ir	2	1	Pr	Ph	H	sPh	H	H	CH3	CH3
529	Ir	2	1	Pr	Tn1	Ph	H	H	H	CH3	CH3

[0059] Hereinbelow, the present invention will be described more specifically based on Examples.

Examples 1 - 6

[0060] Each of luminescence devices having a layer structure shown in Figure 1B were prepared in the following manner.

[0061] On a 1.1 mm-thick glass substrate (transparent substrate 15), a 100 nm-thick film (transparent electrode 14) of ITO (indium tin oxide) was formed by sputtering, followed by patterning to form a stripe electrode including 100 lines each having a width of 100 nm and a spacing with an adjacent line of 10 nm (i.e., electrode pitch of 110 nm).

[0062] On the ITO-formed substrate, three organic layers and two metal electrode layers shown below were successively formed by vacuum (vapor) deposition using resistance heating in a vacuum chamber (10^{-4} Pa).

Organic layer 1 (hole transport layer 13) (40 nm): α -NPD

Organic layer 2 (luminescence layer 12) (30 nm): co-deposited film of CBP:metal complex (metal coordination compound shown in Table 20) (95:5 by weight)

Organic layer 3 (electron transport layer 16) (30 nm): Alq3

Metal electrode layer 1 (metal electrode 11) (15 nm): Al-Li alloy (Li = 1.8 wt. %)

Metal electrode layer 2 (metal electrode 11) (100 nm): Al

[0063] The above-deposited metal electrode layers 1 and 2 (Al-Li layer and Al layer) had a stripe electrode pattern including 100 lines each having a width of 100 nm and a spacing of 10 nm (electrode pitch = 110 nm) and arranged so that the stripe electrode pattern intersected with that of the ITO electrode at right angles to form a matrix of pixels each having an effective electrode area of 3 mm² comprising 20 ITO lines bundled together at a lead-out portion and

15 Al (Al-Li) lines bundled together at a lead-out portion.

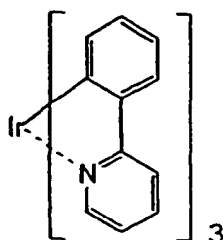
[0064] Each of the thus-prepared luminescence devices was taken out of the vacuum chamber and was subjected to a continuous energization (current passage) test in an atmosphere of dry nitrogen gas stream so as to remove device deterioration factors, such as oxygen and moisture (water content).

5 [0065] The continuous energization test was performed by continuously applying a voltage at a constant current density of 50 mA/cm² to the luminescence device having the ITO (transparent) electrode (as an anode) and the Al (metal) electrode (as a cathode), followed by measurement of emission luminance (brightness) with time so as to determine a time (luminance half-life) required for decreasing an initial luminance (60 - 220 cd/m²) to 1/2 thereof.

[0066] The results are shown in Table 18 appearing hereinafter.

10 Comparative Example 1

[0067] A comparative luminescence device was prepared and evaluated in the same manner as in Examples 1 - 6 except that the Ir complexes (metal coordination compounds shown in Table 20) was changed to Ir-phenylpyrimidine complex (Ir(ppy)₃) shown below.



30 [0068] The results are also shown in Table 18 below.

Table 18

Ex. No.	Compound No.	Luminance half-life (Hr)
Ex. 1	3	450
Ex. 2	11	550
Ex. 3	22	500
Ex. 4	43	500
Ex. 5	45	600
Ex. 6	385	400
Ex. 7	413	650
Comp.Ex. 1	Ir(ppy) ₃	300

45 [0069] As is apparent from Table 18, compared with the conventional luminescence device using Ir(ppy)₃, the luminescence devices using the metal coordination compounds of formula (1) according to the present invention provide longer luminance half-lives, thus resulting in an EL device having a high durability (luminance-stability) based on a good stability of the metal coordination compound of formula (1) of the present invention.

50 Example 7

[0070] A color organic EL display apparatus shown in Figure 2 was prepared in the following manner.

[0071] An active matrix substrate had a planar structure basically similar to a structure described in U.S. Patent No. 6,114,715.

55 [0072] Specifically, on a 1.1 mm-thick glass substrate, top state-type TFTs of polycrystalline silicon were formed in an ordinary manner and thereon, a flattening film was formed with contact holes for electrical connection with a pixel electrode (anode) at respective source regions, thus preparing an active matrix substrate with a TFT-circuit.

[0073] On the active matrix substrate, a 700 nm-thick pixel electrode (anode) of ITO having a larger work function

was formed in a prescribed pattern. On the ITO electrode, prescribed organic layers and a 100 nm-thick Al electrode (cathode) were successively formed by vacuum deposition with a hard mask, followed by patterning to form a matrix of color pixels (128x128 pixels).

[0074] The respective organic layers corresponding to three color pixels (red (R) green (G) and blue (B)) were consisting of the following layers.

<R pixel region>

[0075] α -NPD (40 nm)/CBP: Ex. Comp. No. 22 (93:7 by weight) (30 nm)/BCP (20 nm)/Alq 3 (40 nm)

<G pixel region>

[0076] α -NPD (50 nm)/Alq 3 (50 nm)

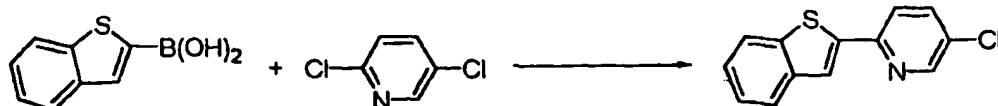
<B pixel region>

[0077] α -NPD (50 nm)/BCP (20 nm)/Alq 3 (50 nm)

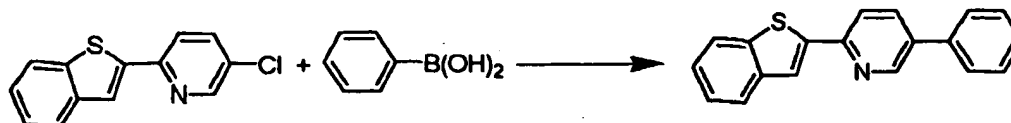
[0078] When the thus-prepared color organic EL display apparatus was driven, desired color image data can be displayed stably with good image qualities.

Example 8 (Synthesis of Example Compound No. 22)

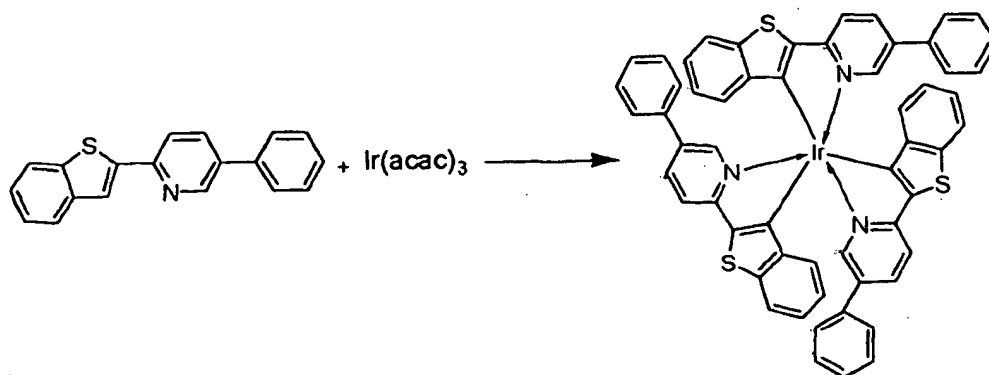
[0079]



[0080] In a 500 ml-three-necked flask, 12.6 g (85.2 mM) of 2,5-dichloropyridine, 15.2 g (85.4 mM) of benzo[*b*]thiophene-2-boronic acid, 75 ml of toluene, 37.5 ml of ethanol and 75 ml of 2M-sodium carbonate aqueous solution were placed and stirred at room temperature under nitrogen stream, and 3.06 g (2.64 mM) of tetrakis(triphenylphosphine)palladium (0) was added thereto, followed by refluxing under stirring for 8 hours under nitrogen stream. After the reaction, the reaction mixture was cooled on an ice bath to precipitate a crystal, which was then filtered out and washed with water. To the crystal, 100 ml of methanol was added and washed under stirring at room temperature, followed by filtration to recover the crystal. The crystal was purified by silica gel column chromatography (eluent: chloroform) and recrystallized from a mixture solvent of chloroform-methanol to obtain 11.8 g (Yield: 56.4 %) of 5-chloro-2-(benzo[*b*]thienyl)pyridine (colorless crystal).



[0081] In a 100 ml-three-necked flask, 4.91 g (20.0 mM) of 5-chloro-2-(benzo[*b*]thienyl)pyridine, 3.66 g (30.0 mM) of phenylboronic acid, 9.58 g (40.0 mM) of tripotassium phosphate hydrate, 3.2 mg (0.020 mM) of palladium (II) acetate, 11.9 mg (0.040 mM) of 2-di-*tert*-butylphosphinobiphenyl and 60 ml of toluene were placed and refluxed under stirring for 24 hours at 100 °C under nitrogen stream. After the reaction, the reaction mixture was cooled on an ice bath to precipitate a crystal, which was then filtered out and washed with water. To the crystal, 25 ml of methanol was added and washed under stirring at room temperature, followed by recovery by filtration. The crystal was purified by silica gel column chromatography (eluent: chloroform) and recrystallized from a chloroform-methanol mixture solvent to obtain 1.17 g (Yield: 20.4 %) of 2-(benzo[*b*]thienyl)-5-phenylpyridine (colorless crystal).



[0082] In a 100 ml-four-necked flask, 50 ml of glycerol was placed and heated at 130 - 140 °C under stirring and bubbling with nitrogen for 2 hours. Then, the glycerol was cooled by standing to 100 °C, and 1.15 g (4.00 mM) of 2-(benzo[b]thienyl)-5-phenylpyridine and 0.40 g (0.82 mM) of iridium (III) acetylacetonate were added thereto, followed by stirring for 5 hours at 180 - 235 °C under nitrogen stream. The reaction mixture was cooled to room temperature and poured into 300 ml of 1N-hydrochloric acid to form a precipitate. The precipitate was recovered by filtration and washed with water, followed by drying for 5 hours at 100 °C under reduced pressure. The resultant precipitate was silica gel column chromatography (eluent: chloroform) to obtain 0.26 g (Yield: 30.2 %) of red powdery tris[2-(benzo[b]thienyl)-5-phenylpyridine-C²,N]iridium (III).

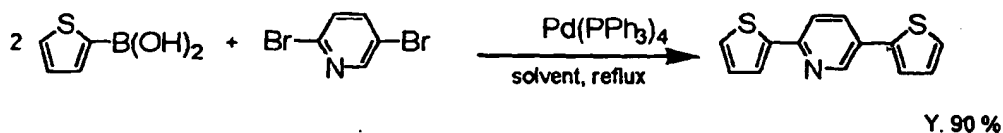
[0083] According to MALDI-TOF MS (matrix-assisted laser desorption ionization-time of flight mass spectroscopy), the compound exhibited M⁺ (mass number of the corresponding cation formed by removal of 1 electron) of 1051.2, thus confirming the objective iridium complex.

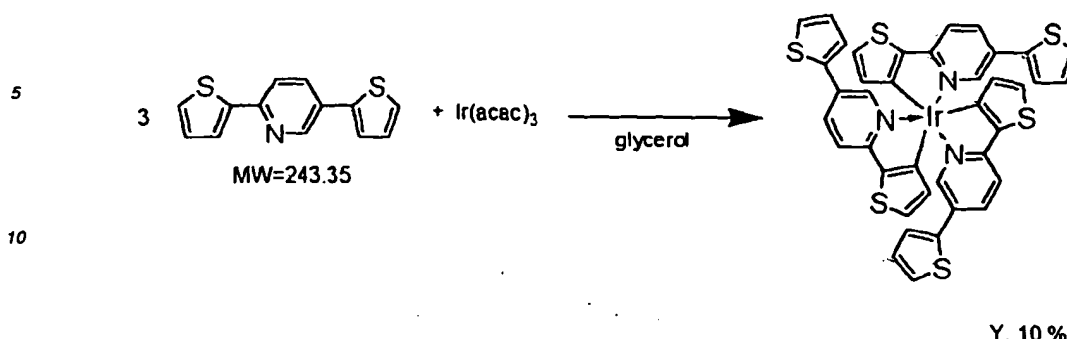
[0084] When the compound was dissolved in toluene and subjected to measurement of phosphorescence spectrum at an excited light wavelength of 380 nm by using a fluorescence spectrometer, the compound exhibited a phosphorescence spectrum showing λ_{max} (maximum emission wavelength) of 620 nm, thus confirming clear red luminescence.

[0085] When the luminescence device prepared in 5 Example 3 using the above-synthesized metal coordination compound (Ex. Comp. No. 22) was subjected to measurement of phosphorescence spectrum in a similar manner, a clear red luminescence was confirmed similarly as in the case of the compound in toluene 0 described above.

Example 9 (Synthesis of Ex. Comp. No. 11)

[0086] A metal coordination compound (Ex. Comp. No. 11) was synthesized through the following reaction schemes. Hereinafter, the synthesis yield is simply represented by "Y".





15 [0087] According to MALDI-TOF MS, the compound exhibited $M^+ = 919.0$, thus being identified as the objective iridium compound.

[0088] When the compound was dissolved in toluene and subjected to measurement of phosphorescence spectrum at an excited light wavelength of 400 nm by using a fluorescence spectrometer, the compound exhibited a phosphorescence spectrum showing λ_{max} (maximum emission wavelength) of 612 nm, thus confirming clear red luminescence.

20 [0089] When a luminescence device having a layer structure shown below and using the above-synthesized metal coordination compound (Ex. Comp. No. 11) was prepared and subjected to measurement of phosphorescence spectrum in a similar manner, a clear red luminescence was confirmed similarly as in the case of the compound in toluene described above.

[0090] ITO (100 nm)/ α -NPD (40 nm)/CBP: Ex. Comp. No. 11 (95:5 by weight)(30 nm)/BCP (20 nm)/Alq3 (40 nm)/Al-Li (1 nm)/Al (100 nm).

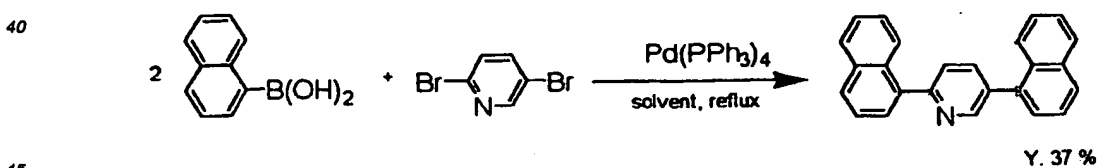
25 [0091] Further, the luminescence device exhibited a good rectifying characteristic.

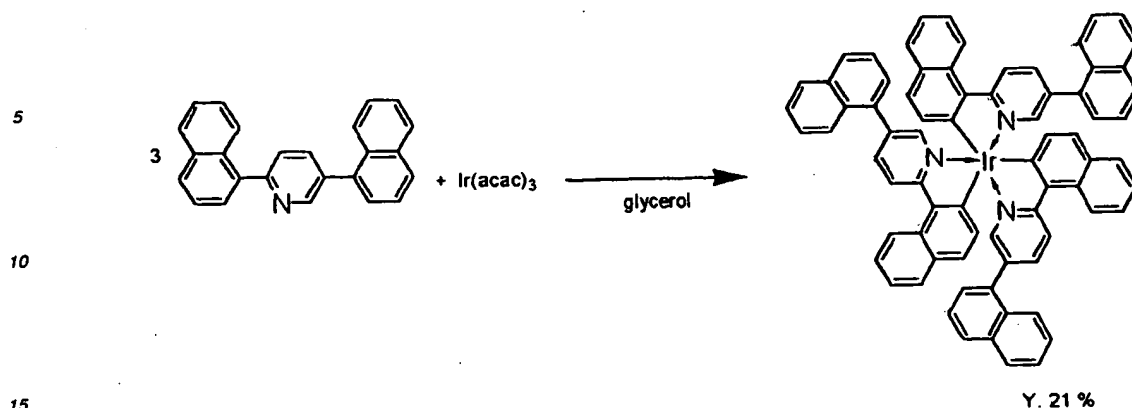
[0092] Specifically, Figure 3A is a graph showing a relationship between an electric field strength (E) and a current density of the luminescence device, and Figure 3B is a graph showing a relationship between an electric field strength (E) and a luminance (L) of the luminescence device. Further, Figure 3C shows a luminescence spectrum of the luminescence device under application of a voltage of 10 volts.

30 [0093] The luminescence device exhibited a luminescence efficiency of 0.8 lm/W under application of a voltage of 10 volts. The luminescence device also emitted stable luminescence even when the luminescence device was continuously supplied with the voltage for ca. 200 hours.

35 Example 10 (Synthesis of Ex. Comp. No. 45)

[0094] A metal coordination compound (Ex. Comp. No. 45) was synthesized through the following reaction schemes.





[0095] According to MALDI-TOF MS, the compound exhibited $M^+ = 1183.3$, thus being identified as the objective iridium compound.

20 [0096] When the compound was dissolved in toluene and subjected to measurement of phosphorescence spectrum at an excited light wavelength of 380 nm by using a fluorescence spectrometer, the compound exhibited a phosphorescence spectrum showing λ_{\max} (maximum emission wavelength) of 603 nm, thus confirming clear reddish orange luminescence.

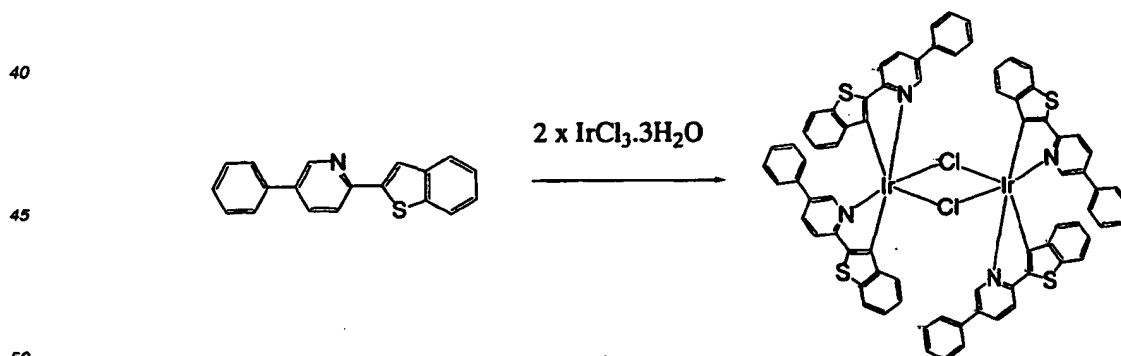
25 [0097] When the luminescence device prepared in Example 5 using the above-synthesized metal coordination compound (Ex. Comp. No. 45) was subjected to measurement of phosphorescence spectrum in a similar manner, a clear reddish orange luminescence was confirmed similarly as in the case of the compound in toluene described above.

[0098] Further, the luminescence device exhibited a good rectifying characteristic.

30 [0099] The luminescence device exhibited a luminescence efficiency of 0.5 lm/W under application of a voltage of 8 volts. The luminescence device also emitted stable luminescence even when the luminescence device was continuously supplied with the voltage for ca. 150 hours.

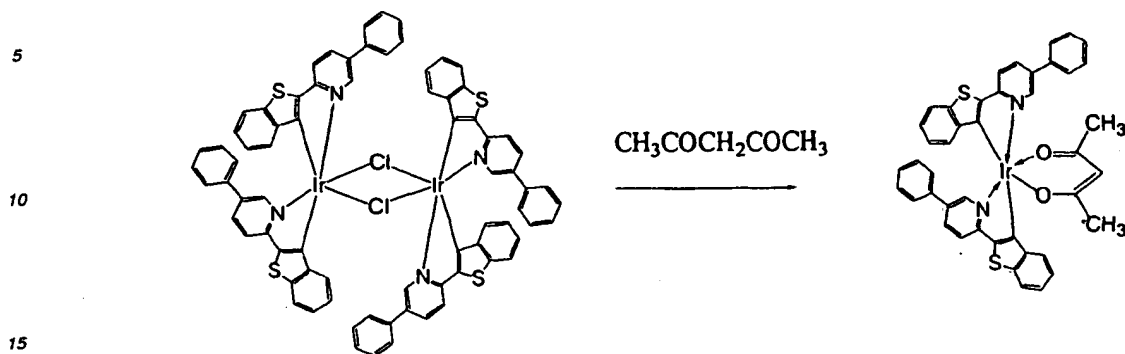
Example 11 (Another synthesis of Ex. Comp. No. 22)

35 [0100] Tris[2-(benzo[b]thienyl)-5-phenylpyridine- C^2,N]iridium (III) (Ex. Comp. No. 22) prepared in Example 8 was synthesized through another reaction schemes shown below.

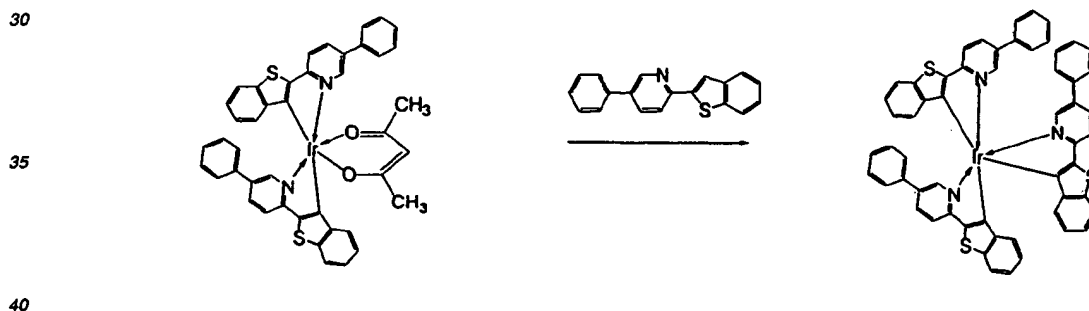


55 [0101] In a 200 ml-three-necked flask, 0.58 mg (1.64 mmole) of iridium (III) chloride-trihydrate (made by Across Organics Co.), 1.5 g (5.22 mmole) of 2-(benzo[b]thienyl)-5-phenylpyridine, 45 ml of ethoxyethanol and 15 ml of water were placed and stirred for 30 min. at room temperature under nitrogen stream, followed by 24 hours of reflux under stirring. The reaction product was cooled to room temperature, and the precipitate was recovered by filtration and washed with water, followed successive washing with ethanol and acetone. After drying under a reduced pressure at room temperature, 1.02 g of red powdery tetrakis[2-(benzo[b]thienyl)-5-phenylpyridine- C^2,N]- $(\mu$ -dichloro)diiridium-(III)

was obtained.



20 **[0102]** In a 200 ml-three-necked flask, 70 ml of ethoxyethanol, 0.95 g (0.72 mmole) of tetrakis[2-(benzo[b]thienyl)-5-phenylpyridine-C²,N](μ-dichloro)-diiridium (III), 0.22 g (2.10 mM) of acetylacetone and 1.04 g (9.91 mM) of sodium carbonate, were placed and stirred for 1 hour at room temperature under nitrogen stream and then refluxed under stirring for 15 hours. The reaction product was cooled with ice, and the precipitate was filtered out and washed with water. The precipitate was then purified by silica gel column chromatography (eluent: chloroform/methanol = 30/1) to obtain 0.43 g of red powdery bis[2-(benzo[b]thienyl)-5-phenylpyridine-C²,N](acetylacetonato)-iridium (III) (Example Compound No. 517). According to MALDI-TOF MS, M⁺ of 864.2 of the compound was confirmed. A toluene solution of the compound exhibited a luminescence spectrum showing λ_{max} = 631 nm and a quantum yield of 0.18 relative to 1.0 of Ir(ppy)₃.



45 **[0103]** In a 100 ml-three-necked flask, 0.27 g (0.94 mM) of 2-(benzo[b]thienyl)-5-phenylpyridine, 0.36 g (0.42 mM) of bis[2-(benzo[b]thienyl)-5-phenylpyridine-C²,N](acetylacetonato)iridium (III) and 25 ml of glycerol, were placed and heated around 180 °C for 8 hours under stirring and nitrogen stream. The reaction product was cooled to room temperature and poured into 170 ml of 1N-hydrochloric acid, and the precipitate was filtered out, washed with water and dried at 100 °C under a reduced pressure for 5 hours. The precipitate was purified by silica gel column chromatography with chloroform as the eluent to obtain 0.27 g of red powdery tris[2-(benzo[g]thienyl)-5-phenylpyridine-C²,N]iridium (III) (Example Compound No. 22). According to MALDI-TOF MS, M⁺ of 1051.2 of the compound was confirmed. A toluene solution of the compound exhibited a luminescence spectrum showing λ_{max} = 627 nm and a quantum yield of 0.17 relative to 1.0 of Ir(ppy)₃.

50 **[0104]** The above-synthesized compound and a luminescence device prepared by using the compound exhibited luminescence characteristics similar to those of the compound and luminescence device prepared in Example 8.

55 **[0105]** Bis[2-(benzo[g]thienyl)-5-phenylpyridine-C²,N]iridium (III) (Ex. Comp. No. 517) prepared in this example as an intermediate product exhibited λ_{max} which was longer by ca. 4 nm than that of the final product (Ex. Comp. No. 22) having three identical ligands. Further, when a luminescence device using the intermediate product was prepared and evaluated in the same manner as in Example 8, the luminescence device exhibited a luminescence spectrum showing λ_{max} = 631 nm. Accordingly, the intermediate product used in this example can also be used as a luminescence material.

Example 12 (Another synthesis of Ex. Comp. No. 45)

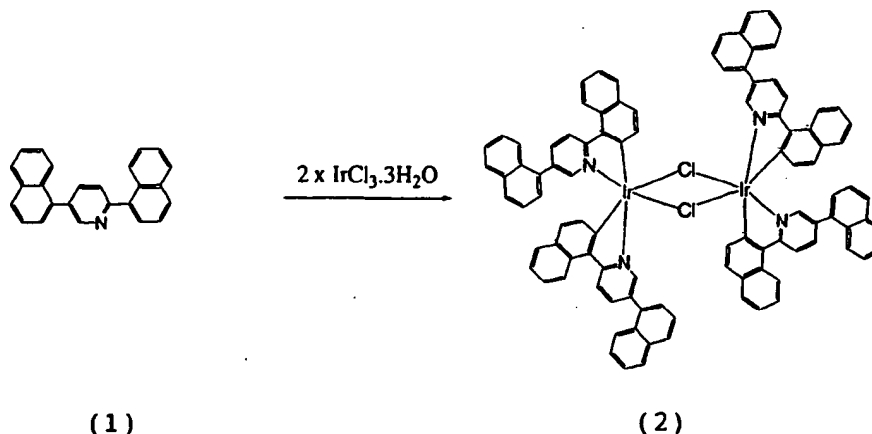
[0106] The metal coordination compound (Ex. Comp. No. 45) prepared in Example 10 was synthesized through another reaction schemes shown below.

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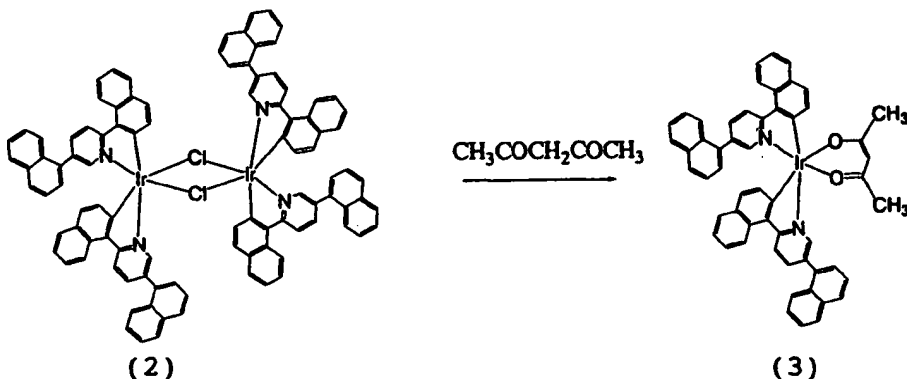
[0107] In a 200 ml-three-necked flask, 0.58 mg (1.64 mmole) of iridium (III) chloride-trihydrate (made by Across Organics Co.), 1.7 g (5.1 mmole) of a compound (1), 45 ml of ethoxyethanol and 15 ml of water were placed and stirred for 30 min. at room temperature under nitrogen stream, followed by 24 hours of reflux under stirring. The reaction product was cooled to room temperature, and the precipitate was recovered by filtration and washed with water, followed successive washing with ethanol and acetone. After drying under a reduced pressure at room temperature, 1.0 g (yield = 93.4 %) of red powdery compound (2) was obtained.

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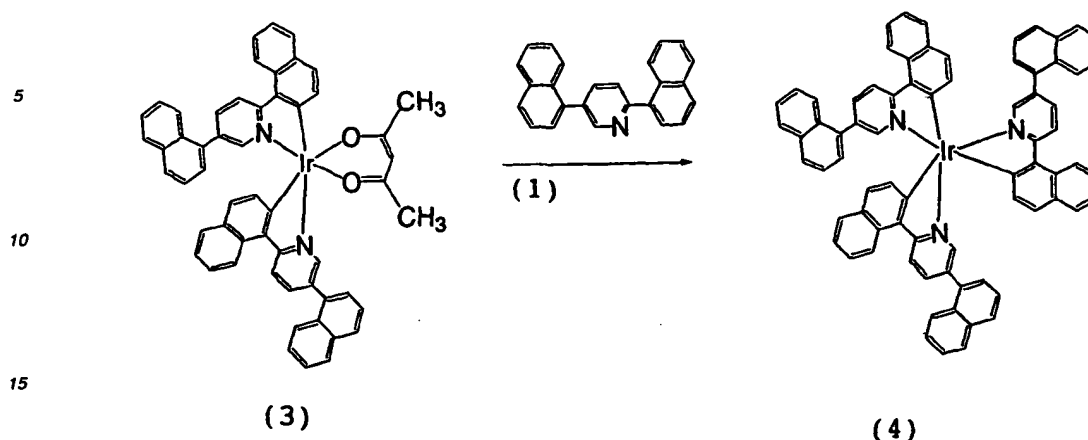
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[0108] In a 200 ml-three-necked flask, 70 ml of ethoxyethanol, 0.90 g (0.71 mmole) of the compound (2), 0.22 g (2.10 mmole) of acetylacetone and 1.04 g (9.91 mmole) of sodium carbonate, were placed and stirred for 1 hour at room temperature under nitrogen stream and then refluxed under stirring for 15 hours. The reaction product was cooled with ice, and the precipitate was filtered out and washed with water. The precipitate was then purified by silica gel column chromatography (eluent: chloroform/methanol = 30/1) to obtain 0.39 g of red powdery compound (3) (Example Compound No. 519). According to MALDI-TOF MS, M^+ of 952.3 of the compound was confirmed. A toluene solution of the compound exhibited a luminescence spectrum showing λ_{\max} = 608 nm and a higher quantum yield of 0.30 relative to 1.0 of Ir(ppy)₃ in this emission wavelength region.



20 **[0109]** In a 100 ml-three-necked flask, 0.29 g (0.88 mM) of the compound (1) 0.34 g (0.35 mM) of the compound (3) and 25 ml of glycerol, were placed and heated around 180 °C for 8 hours under stirring and nitrogen stream. The reaction product was cooled to room temperature and poured into 170 ml of 1N-hydrochloric acid, and the precipitate was filtered out, washed with water and dried at 100 °C under a reduced pressure for 5 hours. The precipitate was purified by silica gel column chromatography with chloroform as the eluent to obtain 0.23 g of red powdery compound

25 (4) (Example Compound No. 45). According to MALDI-TOF MS, M^+ of 1183.4 of the compound was confirmed. A toluene solution of the compound exhibited a luminescence spectrum showing $\lambda_{\max} = 603$ nm and a quantum yield of 0.278 relative to 1.0 of Ir(ppy)₃.

[0110] The above-synthesized compound and a luminescence device prepared by using the compound exhibited luminescence characteristics similar to those of the compound and luminescence device prepared in Example 10.

30 **[0111]** The compound (3) (Ex. Comp. No. 519) prepared in this example as an intermediate product exhibited λ_{\max} which was longer by ca. 4 nm than that of the final product (Ex. Comp. No. 45) having three identical ligands. Further, when a luminescence device using the intermediate product was prepared and evaluated in the same manner as in Example 10, the luminescence device exhibited a luminescence spectrum showing $\lambda_{\max} = 608$ nm and an external luminescence yield of 0.7 lm/W. Further, the luminescence device emitted stable luminescence even when continuously

35 supplied with the voltage for ca. 100 hours. Accordingly, the intermediate product used in this example can also be used as a luminescence material.

Example 13 (Synthesis of Ex. Comp. Nos. 520 and 525)

40 **[0112]** It is easy to synthesize the following compounds in the same manner as in Example 11-except that 4-chloro-pyrimidine is synthesized from 4(3H)-pyrimidone (made by Aldrich Co.) in the same manner as the process described at pages 37 and 38 of JP-A (Tokuhyo) 2001-504113 (corr. to U.S. Patent No. 6,300,330) and is reacted with 4-phenylboronic acid (made by Lancaster Co.) to obtain 4-(biphenyl-4-yl)pyrimidine, which is used instead of 2-(benzo[b]thienyl)-5-phenylpyridine.

45 **[0113]** Bis[4-(biphenyl-4-yl)pyrimidine- C^3, N^3](acetylacetonato)iridium (III) (Ex. Comp. No. 520).

[0114] Tris[4-(biphenyl-4-yl)pyrimidine- C^3, N^3]iridium (III) (Ex. Comp. No. 525).

Example 14 (Synthesis of Ex. Comp. Nos. 521 and 526)

50 **[0115]** It is easy to synthesize the following compounds in the same manner as in Example 11 except that 4-(4-chlorophenyl)pyrimidine is synthesized from 4-chloropyrimidine prepared in Example 13 and 4-chlorophenylboronic acid (made by Aldrich Co.) and was reacted with 2-naphthaleneboronic acid (made by Lancaster Co.) to obtain 4-[4-(2-naphthyl)phenyl]-pyrimidine, which is used instead of 2-(benzo[b]thienyl)-5-phenylpyridine.

[0116] Bis[4-[4-(2-naphthyl)phenyl]pyrimidine- C^3, N^3](acetylacetonato)iridium (III) (Ex. Comp. No. 521).

55 **[0117]** Tris[4-[4-(2-naphthyl)phenyl]pyrimidine- C^3, N^3]iridium (III) (Ex. Comp. No. 526).

Example 15 (Synthesis of Ex. Comp. Nos. 522 and 527)

[0118] It is easy to synthesize the following compounds in the same manner as in Example 11 except that 2,4-diphenylpyridine is synthesized from phenylboronic acid (made by Tokyo Kasei Kogyo K.K.) and 4-phenyl-2-bromopyridine (made by General Intermediates of Canada) and was used instead of 2-(benzo[b]thienyl)-5-phenylpyridine.

[0119] Bis(2,4-diphenylpyridine-C²,N¹)(acetylacetonato)iridium (III) (Ex. Comp. No. 522).

[0120] Tris(2,4-diphenylpyridine-C²,N¹)iridium (III) (Ex. Comp. No. 527).

Example 16 (Synthesis of Ex. Comp. Nos. 523 and 528)

[0121] It is easy to synthesize the following compounds in the same manner as in Example 11 except that 2-(biphenyl-3-yl)pyridine is synthesized from 3-biphenylboronic acid (made by Lancaster Co.) and 2-bromopyridine (made by Tokyo Kasei Kogyo K.K.) and is used instead of 2-(benzo[b]thienyl)-5-phenylpyridine.

[0122] Bis[2-(biphenyl-3-yl)pyridine-C⁴,N³](acetylacetonato)iridium (III) (Ex. Comp. No. 523).

[0123] Tris[2-(biphenyl-2-yl)pyridine-C⁴,N³]iridium (III) (Ex. Comp. No. 528).

Example 17 (Synthesis of Ex. Comp. Nos. 524 and 529)

[0124] It is easy to synthesize the following compounds in the same manner as in Example 11 except that 2-(5-bromothiophene-2-yl)pyridine is synthesized from 2-bromopyridine (made by Tokyo Kasei Kogyo K.K.) and 5-bromothiophene-2-boronic acid (made by Aldrich Co.) and was reacted with phenylboronic acid (made by Tokyo Kasei Kogyo K.K.) to obtain 2-(5-phenylthiophene-2-yl)pyridine, which is used instead of 2-(benzo[b]thienyl)-5-phenylpyridine.

[0125] Bis[2-(5-phenylthiophene-2-yl)pyridine-C²,N¹](acetylacetonato)iridium (III) (Ex. Comp. No. 524).

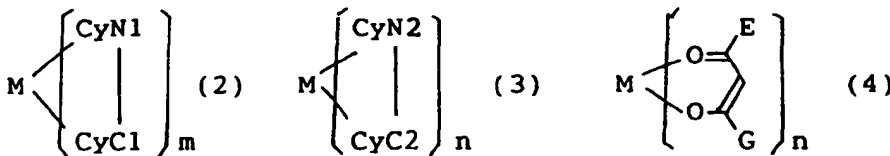
[0126] Tris[2-(5-phenylthiophene-2-yl)pyridine-C²,N¹]iridium (III) (Ex. Comp. No. 529).

[0127] As described above, according to the present invention, the metal coordination compound of the formula (1) characterized by aromatic substituent. The electroluminescence device (luminescence device) of the present invention using, as a luminescent center material, the metal coordination compound of the formula (1) is an excellent device which not only allows high-efficiency luminescence but also retains a high luminance for a long period and shows little deterioration by current passage. Further, the display apparatus using the electroluminescence device of the present invention exhibits excellent display performances.

[0128] An electroluminescence device having a layer containing a specific metal coordination compound is provided. The metal coordination compound is represented by formula (1) below:



wherein M is a metal atom of Ir, Pt, Rh or Pd; L and L' are mutually different bidentate ligands; m is 1, 2 or 3 and n is 0, 1 or 2 with the proviso that m+n is 2 or 3; a partial structure ML_m is represented by formula (2) shown below and a partial structure ML'_n is represented by formula (3) or (4) shown below:



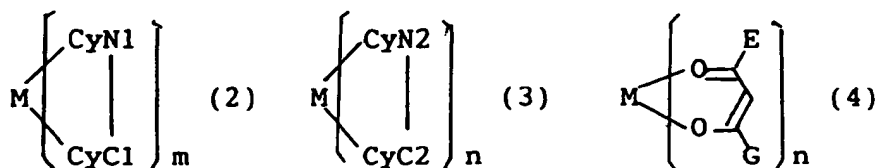
The metal coordination compound of the formula (1) is characterized by having at least one aromatic substituent for at least one of CyN1, CyN2, CyC1 and CyC2. The metal coordination compound having the aromatic substituent is effective in providing high-efficiency luminescence, long-term high luminance, and less deterioration by current passing.

Claims

1. A metal coordination compound represented by formula (1) below:



wherein M is a metal atom of Ir, Pt, Rh or Pd; L and L' are mutually different bidentate ligands; m is 1, 2 or 3 and n is 0, 1 or 2 with the proviso that m+n is 2 or 3; a partial structure ML_m is represented by formula (2) shown below and a partial structure ML'_n is represented by formula (3) or (4) shown below:



wherein CyN1 and CyN2 are each cyclic group capable of having a substituent, including a nitrogen atom and bonded to the metal atom M via the nitrogen atom; CyC1 and CyC2 are each cyclic group capable of having a substituent, including a carbon atom and bonded to the metal atom M via the carbon atom with the proviso that the cyclic group CyN1 and the cyclic group CyC1 are bonded to each other via a covalent bond and the cyclic group CyN2 and the cyclic group CyC2 are bonded to each other via a covalent bond;

the optional substituent of the cyclic groups is selected from a halogen atom, cyano group, a nitro group, a trialkylsilyl group of which the alkyl groups are independently a linear or branched alkyl group having 1 to 8 carbon atoms, a linear or branched alkyl group having 1 to 20 carbon atoms of which the alkyl group can include one or non-neighboring two or more methylene groups that can be replaced with -O-, -S-, -CO-, -CO-O-, -O-CO-, -CH=CH- or -C≡C-, and the alkyl group can include a hydrogen atom that can be optionally replaced with a fluorine atom; or an aromatic group capable of having a substituent which is selected from an aromatic group capable of having a substituent (that is a halogen atom, a cyano atom, a nitro atom, a linear or branched alkyl group having 1 to 20 carbon atoms of which the alkyl group can include one or non-neighboring two or more methylene groups that can be replaced with -O-, -S-, -CO-, -CO-O-, -O-CO-, -CH=CH- or -C≡C-, and the alkyl group can include a hydrogen atom that can be optionally replaced with a fluorine atom), a halogen atom, a cyano atom, a nitro atom, and a linear or branched alkyl group having 1 to 20 carbon atoms (of which the alkyl group can include one or non-neighboring two or more methylene groups that can be replaced with -O-, -S-, -CO-, -CO-O-, -O-CO-, -CH=CH- or -C≡C-, and the alkyl group can include a hydrogen atom that can be optionally replaced with a fluorine atom);

E and G are independently a linear or branched alkyl group having 1 to 20 carbon atoms of which the alkyl group can include a hydrogen atom that can be optionally replaced with a fluorine atom, or an aromatic group capable of having a substituent (that is a halogen atom, a cyano atom, a nitro atom, a trialkylsilyl group of which the alkyl groups are independently a linear or branched alkyl group having 1 to 8 carbon atoms, a linear or branched alkyl group having 1 to 20 carbon atoms of which the alkyl group can include one or non-neighboring two or more methylene groups that can be replaced with -O-, -S-, -CO-, -CO-O-, -O-CO-, -CH=CH- or -C≡C-, and the alkyl group can include a hydrogen atom that can be optionally replaced with a fluorine atom), a halogen atom, a cyano atom, a nitro atom, a linear or branched alkyl group having 1 to 20 carbon atoms of which the alkyl group can include one or non-neighboring two or more methylene groups that can be replaced with -O-, -S-, -CO-, -CO-O-, -O-CO-, -CH=CH- or -C≡C-, and the alkyl group can include a hydrogen atom that can be optionally replaced with a fluorine atom);

the cyclic groups CyN1, CyN2, CyC1 and CyC2 have at least one aromatic substituent capable of having a substituent which is selected from an aromatic group capable of having a substituent (that is a halogen atom, a cyano atom, a nitro atom, a linear or branched alkyl group having 1 to 20 carbon atoms of which the alkyl group can include one or non-neighboring two or more methylene groups that can be replaced with -O-, -S-, -CO-, -CO-O-, -O-CO-, -CH=CH- or -C≡C-, and the alkyl group can include a hydrogen atom that can be optionally replaced with a fluorine atom), a halogen atom, a cyano atom, a nitro atom, a linear or branched alkyl group having 1 to 20 carbon atoms of which the alkyl group can include one or non-neighboring two or more methylene groups that can be replaced with -O-, -S-, -CO-, -CO-O-, -O-CO-, -CH=CH- or -C≡C-, and the alkyl group can include a hydrogen atom that can be optionally replaced with a fluorine atom).

2. A metal coordination compound according to Claim 1, including a partial structure ML'_n represented by the formula (3) in the formula (1).

3. A metal coordination compound according to Claim 1, including a partial structure ML'_n represented by the formula (4) in the formula (1).

4. A metal coordination compound according to Claim 1, wherein n is 0 in the formula (1).
5. A metal coordination compound according to Claim 1, wherein in the formula (2), CyN1 is pyridyl group and CyC1 is naphthyl group.
6. A metal coordination compound according to Claim 1, wherein in the formula (2), CyN1 is pyridyl group and CyC1 is thienyl group.
7. A metal coordination compound according to Claim 1, wherein in the formula (2), CyN1 is pyridyl group and CyC1 is benzothienyl group.
8. An electroluminescence device, comprising: a pair of electrodes disposed on a substrate, and a luminescence unit comprising at least one organic compound disposed between the electrodes, wherein the organic compound comprises a metal coordination compound represented by the formula (1) in Claim 1.
9. A metal coordination compound according to Claim 8, including a partial structure ML'_n represented by the formula (3) in the formula (1).
10. A metal coordination compound according to Claim 8, including a partial structure ML'_n represented by the formula (4) in the formula (1).
11. A metal coordination compound according to Claim 8, wherein n is 0 in the formula (1).
12. An electroluminescence device according to Claim 8, wherein a voltage is applied between the electrodes to emit light.
13. An electroluminescence device according to Claim 8, wherein a voltage is applied between the electrodes to emit phosphorescence.
14. A picture display apparatus, comprising an electroluminescence device according to Claim 8, and a means for supplying electric signals to the electroluminescence device.

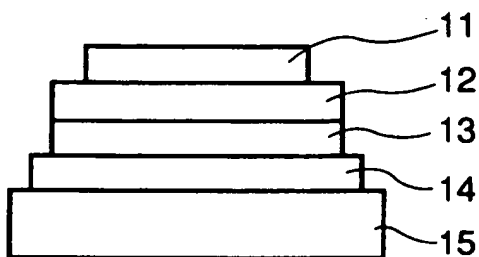


FIG. 1A

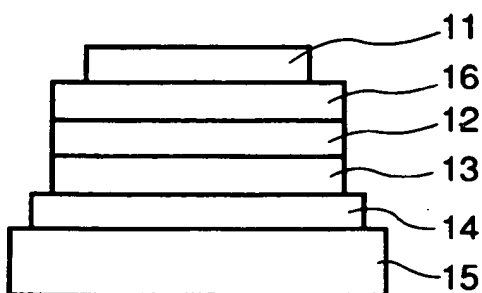


FIG. 1B

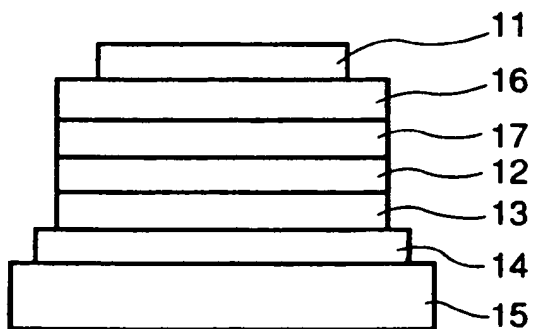


FIG. 1C

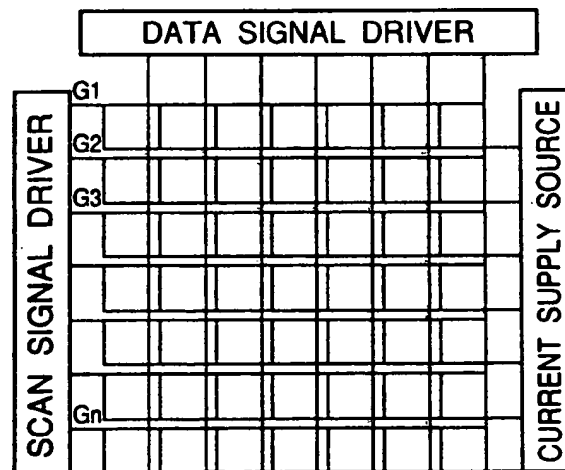


FIG. 2

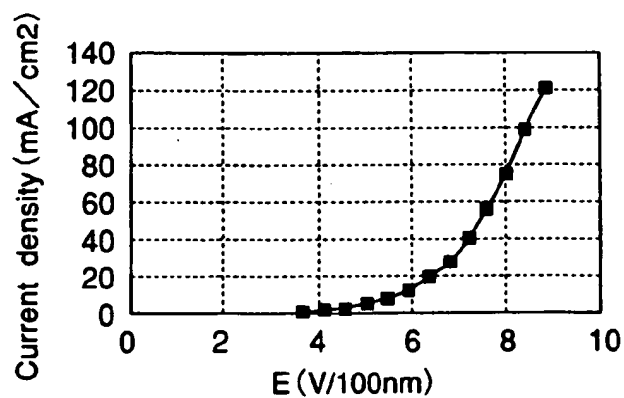


FIG. 3A

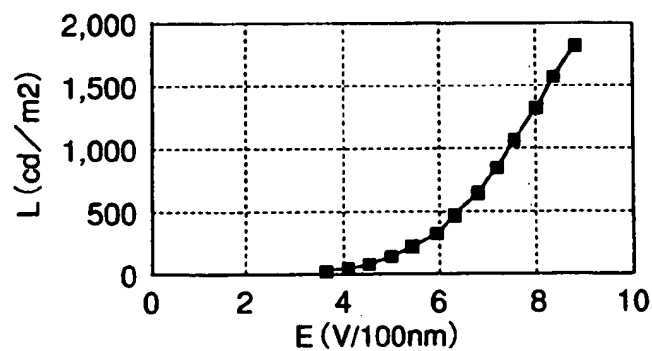


FIG. 3B

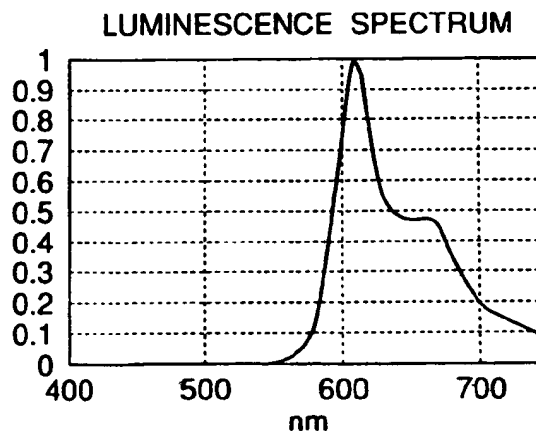


FIG. 3C



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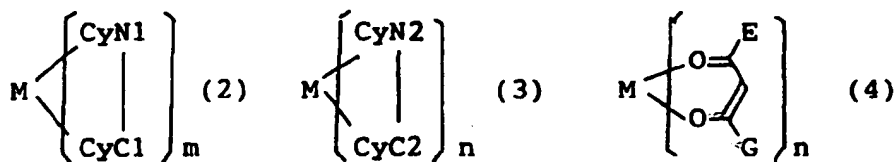
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(54) **Metal coordination compound, luminescence device and display apparatus**

(57) An electroluminescence device having a layer containing a specific metal coordination compound is provided. The metal coordination compound is represented by formula (1) below:



wherein M is a metal atom of Ir, Pt, Rh or Pd; L and L' are mutually different bidentate ligands; m is 1, 2 or 3 and n is 0, 1 or 2 with the proviso that m+n is 2 or 3; a partial structure ML_m is represented by formula (2) shown below and a partial structure ML'_n is represented by formula (3) or (4) shown below:



The metal coordination compound of the formula (1) is characterized by having at least one aromatic substituent for at least one of CyN1, CyN2, CyC1 and CyC2. The metal coordination compound having the aromatic substituent is effective in providing high-efficiency luminescence, long-term high luminance, and less deterioration by current-passing.

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EUROPEAN SEARCH REPORT

Application Number
EP 02 00 5113

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
E	EP 1 191 612 A (CANON KK) 27 March 2002 (2002-03-27) * the whole document *	1,2,4-9, 11-14	H01L51/30 C07F15/00 H01L51/00
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Application Number

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CLAIMS INCURRING FEES

The present European patent application comprised at the time of filing more than ten claims.

- ☐ Only part of the claims have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims and for those claims for which claims fees have been paid, namely claim(s):
- ☐ No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims.

LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

see sheet B

- ☒ All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.
- ☐ As all searchable claims could be searched without effort justifying an additional fee, the Search Division did not invite payment of any additional fee.
- ☐ Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid, namely claims:
- ☐ None of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims, namely claims:



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LACK OF UNITY OF INVENTION
SHEET B

Application Number

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The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

1. claims: 2,4,9,11; partially 1,5,6-8,12-14

Metal coordination compound of formula (1) wherein ML'n is represented by formula (3), electroluminescent device comprising such a coordination compound and picture display comprising the device.

2. claims: 3,10; partially 1,5-8,12-14

Metal coordination compound of formula (1) wherein ML'n is represented by formula (4), electroluminescent device comprising such a coordination compound and picture display comprising the device.

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